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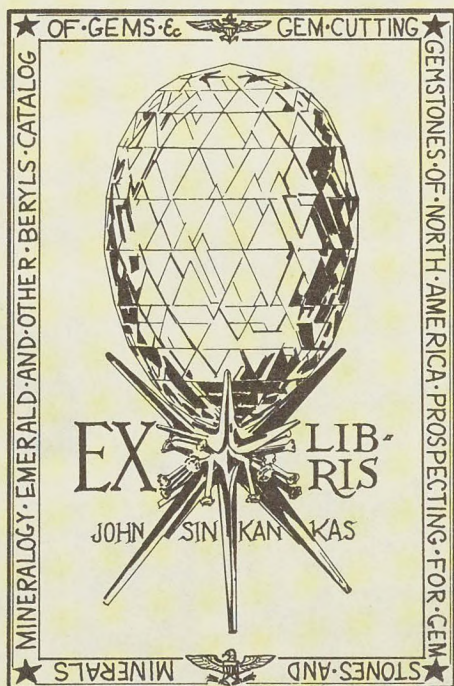
DIOPSIDE AND ITS RELATIONS TO CALCIUM
AND MAGNESIUM METASILICATES.

By E. T. ALLEN and W. P. WHITE

WITH OPTICAL STUDY.

By FRED. EUGENE WRIGHT and ESER S. LARSEN

(With Plate I.)



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[FOURTH SERIES.]

ART. I.—*Diopside and its Relations to Calcium and Magnesium Metasilicates*; by E. T. ALLEN and W. P. WHITE.
With Optical Study; by FRED. EUGENE WRIGHT and
ESPER S. LARSEN. (With Plate I.)

THE pyroxenes were chosen some time since as a good subject for laboratory investigation, both by reason of their geologic importance and because their comparative stability and simplicity of composition seemed to offer relatively little difficulty in their synthesis and study. Diopside is the simplest of this group of minerals, but before even this could be studied satisfactorily, a detailed investigation of both calcium and magnesium metasilicates was found necessary, a full account of which has been given elsewhere.* Here it will be sufficient to state that calcium silicate exists in two crystal forms, one of which, the mineral wollastonite (β -form), is stable up to about 1190° , when it reverts to a pseudo-hexagonal form (α -form) which melts at 1512° . The case of magnesium metasilicate is more complex. There is one form (monoclinic) strongly resembling the pyroxenes, both optically and crystallographically, which is stable up to 1365° (β -form). Here it passes over into an orthorhombic form (α -form) recalling forsterite (Mg_2SiO_4) in its habit and optical properties. It melts at 1524° . Three other forms exist, viz., the minerals enstatite, kufferite, and a monoclinic amphibole similar to the latter. All are monotropic, and change into the β -form when heated to a sufficiently high temperature.

The question of the relation of diopside to its component salts, calcium and magnesium silicate, we undertook to settle by determinations of the melting point and specific volume

* Allen, White and Wright, this Journal, xxi, 89, 1906; Allen, Wright and Clement, this Journal, xxii, 385, 1906. Their form, then undiscovered, is described for the first time in these pages.

curves, relying on very careful microscopic examinations to make sure of the solid phases which separated from the molten solutions. Since we are concerned here with *equilibrium* conditions, it will be evident that the monotropic forms of magnesium silicate do not enter into the problem.* In addition to this specific problem, viz., the relations existing between the calcium and magnesium silicates, we planned to study the most important properties of diopside and its transformations on heating, if any.

Many of the methods used in this investigation have been already described in previous papers from this laboratory;† others have been devised in the course of the work.

Preparation of the Mixtures.—Quartz, magnesia and calcium carbonate were mixed in the proper proportions and melted in large covered platinum crucibles. The molten charges were chilled by dipping the crucibles into water, cracked out of the crucibles, crushed fine, and remelted to ensure thorough mixing. All the materials were carefully examined for impurities, and we are able to state with certainty that the products contained no more than 0.1 per cent to 0.2 per cent of foreign matter, except in certain cases where the same preparation was repeatedly melted and crushed, when as much as 0.3 per cent impurity was sometimes found.

We had considerable trouble in getting magnesia sufficiently pure for our purposes. The chief impurity is generally lime, of which all the samples examined by us contained 0.5 per cent or more. At our request, the firm of Baker & Adamson undertook the problem of preparing pure magnesia in quantity, and succeeded in making a "basic carbonate" in which the minimum quantity of lime amounted to about .07 per cent, or 0.15 per cent of the calcined oxide. A sample of magnesium metasilicate prepared from one lot of this carbonate gave by direct test .12 per cent lime. In mixtures very high in magnesia a correction was generally made for this impurity, i. e., the proper deduction was made from the quantity of lime required by the particular mixture in hand. For the sake of control we analyzed two of the preparations and the results are given below.

At one time during the investigation, it was suspected that some loss might be caused by the strong blast of the gas furnace in which the constituent powders were first melted together in spite of the fact that the crucible was carefully covered. The magnesia being by far the lightest of the constituents

*Viktor Pöschl incorrectly designates the series "*enstatite-diopside*," Centr. Min., 1906, p. 572.

†This Journal, xix, 125, 1905; xxi, 89, 1905; Tschermak's Mitth., xxvi, 169, 1907.

(magnesia, calcium carbonate, quartz), its loss would be disproportionate to its weight in the mixture. But the analysis of the 60 per cent MgSiO_3 mixture, in which the magnesia was slightly high, shows that the suspicion was unfounded.

		Found	Cal.
1. 10% MgSiO_3 -----	SiO_2 -----	52.75	52.67
90% CaSiO_3 -----	CaO -----	43.52	43.33
	MgO -----	4.06	4.00
	Fe_2O_3 etc. -----	.11	----
		100.44	100.00
2. 60% MgSiO_3 -----	SiO_2 -----	56.80	56.73
40% CaSiO_3 -----	CaO -----	19.12	19.26
	MgO -----	24.11	24.01
	Fe_2O_3 etc. -----	.13	----
		100.16	100.00

Thermal Study.—The thermal study was carried on, as in other published work from this laboratory, by Frankenheim's method, melting point curves being used exclusively. Freezing-point curves are unreliable on account of the undercooling, which, even in substances which crystallize as readily as the metasilicates of calcium and magnesium, is often considerable. The mixture under investigation was heated in a platinum crucible, in an electric resistance furnace fed from a storage battery, the temperatures were read to tenths of a degree by a Le Chatelier thermoelement and a potentiometer, and evaluated in terms of a standard saturated cadmium cell.

Since the work here described continued over a considerable period of time, the methods used varied somewhat as successive improvements were introduced. In the earlier portion of it, charges of about 25 grams were used, and the thermoelement was protected by a porcelain tube with a platinum jacket. A control element was also employed to detect any irregularity in the heat supply.* Soon after the work was begun, the practice was also instituted of comparing the thermoelements with standards in order to correct for their deterioration,† due to contamination with iridium from the platinum crucibles and furnace coil. This has now been greatly reduced by using specially pure platinum within the furnace, but occasional comparisons with standard elements are still necessary.‡ Frequently the thermoelements were inserted together in the porcelain tube and used to read the same melting point. The

* This Journal, xxi, 94, 1906.

† The Constancy of Thermoelements, W. P. White, Phys. Zeitschr., viii, 325, 1907.

‡ W. P. White, Phys. Rev., xxv, 336, 1907.

readings when separately corrected then seldom varied $\frac{1}{2}^{\circ}$, which was about the accuracy with which any two working elements could be compared. The variations in the results, sometimes amounting to 2° , even with the more sharply melting substances (the end members, the eutectics, and diopside), were therefore due to uncertainty in locating the melting point, and not to the temperature measurements.

In the latter part of the work, charges of only $2\frac{1}{2}$ grams were used, in very small crucibles of pure platinum, in which the naked thermoelements could safely be immersed. Under these conditions and with proper precautions, the variations rarely exceeded $\frac{1}{2}^{\circ}$. The small crucibles could also be more easily moved in the hot furnace, chilled in cold water, etc., and a wider range in the conditions of crystallization obtained. Furthermore, the thermal lag of the diminutive charges was very small, and complex thermal phenomena could be analyzed or separated with much greater certainty than with larger crucibles. The small crucibles were mainly used in investigating those portions of the field in which the interpretation of the phenomena had proved particularly difficult. They were used, however, in a sufficient number of cases to afford a thorough control of the earlier determinations made with 25 grams, and showed that these were accurate within their own accidental errors.

The agreement obtained between observations of the same point in both the earlier and later work is well illustrated in the following table:

TABLE I.

Agreement of Observations in Earlier and Later Work.

Temperatures in microvolts. About 13 microvolts to 1° .			
70% MgSiO ₃ : 30% CaSiO ₃ . 25 gr. charge.		28% MgSiO ₃ : 72% CaSiO ₃ . $2\frac{1}{2}$ gr. charge.	
June, 1905.	14,147	Oct. 1907.	13,772
	130		776
	110		777
	138		779
	148		----
	127		----
	<hr/>		<hr/>
Mean	14,133		13,776
Average deviation,	11 mv.		2 mv.
Extreme “	37 mv.		7 mv.

These particular instances were selected for illustration as being, each in its class, the one showing the largest number of strictly comparable observations. Each one is typical, and

neither is the best that could be given. Each represents three different charges.

A word as to the exact significance of the accuracy here indicated may avoid some confusion.

In comparative measurements with very small crucibles (2.5 grams) and bare thermoelements, the relative accuracy obtainable by the same observer with the same apparatus is $\frac{1}{2}^{\circ}$ or better; with the larger crucibles (25 grams) and jacketed elements, differences may reach 3° . This is shown in Table I, page 4.

The absolute value of the measurements is not established with this accuracy. Different observers, indeed, working independently with different apparatus, ought not to differ much in their results through differences in experimental methods, provided these are not positively faulty; that is, provided the thermal junction is actually at the temperature of the melting material. This is shown by the agreement of our earlier and later results, obtained with highly differing methods, and also, perhaps more conclusively, by the agreement found between Dr. Day's special form of element* and the ordinary jacketed element. Differences between independent observers are, however, to be expected in the thermoelement calibration, particularly at the present time, when a long extrapolation is necessary. Practically all temperature measurements above the melting point of copper (1084° C., Reichsanstalt Scale) are now obtained by extrapolating some simple function which has been experimentally established for temperatures below that point. With the same function and different elements, temperatures usually do not vary more than 2° C. at $1,500^{\circ}$. With different functions, the extrapolated curves may diverge as much as 30° C. at $1,500^{\circ}$. An error of 0.5° in the determination of the copper point itself may cause an error of 4° in the extrapolated curve at $1,500^{\circ}$. All these are differences in the interpretation of the experimental measurements, which will probably continue to cause considerable differences between the results of different observers until the gas thermometer scale is extended to that temperature with sufficient accuracy, after which they can be readily recomputed to the established scale. The temperatures here given are computed from the Reichsanstalt Scale. In brief then, the *accuracy*

* Carnegie Institution Publication No. 31, p. 25. Our value for magnesium silicate is 3° higher than that found by Allen, Wright and Clement, but this difference is only a little greater than the accidental variations occurring in the present work. With charges of the same size, errors in the method seem most likely to occur, if at all, as the result of a very uneven temperature distribution in the furnace or of insufficient immersion of the thermoelement in the charge. In a few cases where the platinum jacket dropped down so as to rest against the bottom of the crucible, which was cooled by contact with the pedestal below it, the melting point came about 5° too low.

of the determinations is shown by comparing the measurements among themselves. Their *interpretation* in terms of an absolute scale depends upon an agreement among observers, and will vary from time to time whenever more accurate fundamental observations are available. At the present time the Reichsanstalt Scale is generally accepted.

The melting points measured, like those obtained in this laboratory with the feldspars, and by workers in high temperatures generally, are not entirely sharp, even with substances which theoretically should melt at a strictly constant temperature. Indications that melting has already begun invariably appear on the thermal curve 20° or 30° below the melting point proper, and the region of strongest absorption of heat is distributed over an interval of from 2° to 3° . The main cause of this phenomenon in the present case probably lies neither in any unusual molecular viscosity attending the change of state* nor in experimental error of the temperature observations. It may be due to the slight impurity ($\cdot 1$ to $\cdot 2$ per cent) which chemical analysis shows to be present, even in the most carefully prepared artificial mixtures. Similar curves are obtained with ice to which 2 per cent or 3 per cent of salt has been added, and at an absolute temperature five or six times as high the same effect should be produced by about one-thirtieth as much impurity.† The highest portion, that is, the end, of the melting interval is taken as the melting point, since this is probably the nearest attainable approach to what would be the sharp melting point of the substance unaffected by traces of impurity.

The Melting Point Curve from 0 per cent—46.3 per cent $MgSiO_3$.—The temperature-time curves were taken on a series of mixtures of the metasilicates 5 per cent to 10 per cent apart except in critical parts of the curve, where shorter intervals were chosen. The temperatures at which the heat absorptions took place are plotted in fig. 1. The results in the case of about one-third of the mixtures were controlled by repeating the observations on several different preparations, and since the thermal phenomena in certain parts of the curve were rather complicated, a considerable number of the observations were many times repeated, making in all nearly four hundred independent determinations.

By reference to the diagram (fig. 1) it will be seen that the addition of magnesium silicate to pure calcium silicate (pseudo-wollastonite) lowers the melting point rapidly, the curve fol-

* This, of course, is not true of the feldspars, quartz, etc.

† In accordance with the Van't Hoff-Raoult formula, where Δ , the depression of the freezing point due to impurity, equals $\frac{\cdot 02 T^2}{\lambda}$.

lowing a slightly curved line to the eutectic point, 1348° , at about 28 per cent magnesium silicate. The curve then rises much more gradually to a maximum of 1380° at the composition of diopside, $\text{CaSiO}_3\cdot\text{MgSiO}_3$, which contains 46.3 per cent magnesium silicate. Let us first consider so much of the curve by itself. The solid phases, which separated when the mixtures from 0 per cent—46.3 per cent magnesium silicate were crystallized as nearly as possible under equilibrium conditions, were proved by microscopic analysis to be only diopside and pseudo-wollastonite, making of course the proper allowance for a small mutual solubility. The latter amounted, as we shall see, to about 3 per cent diopside in the pseudo-wollastonite, and less than 3 per cent of the latter in diopside.

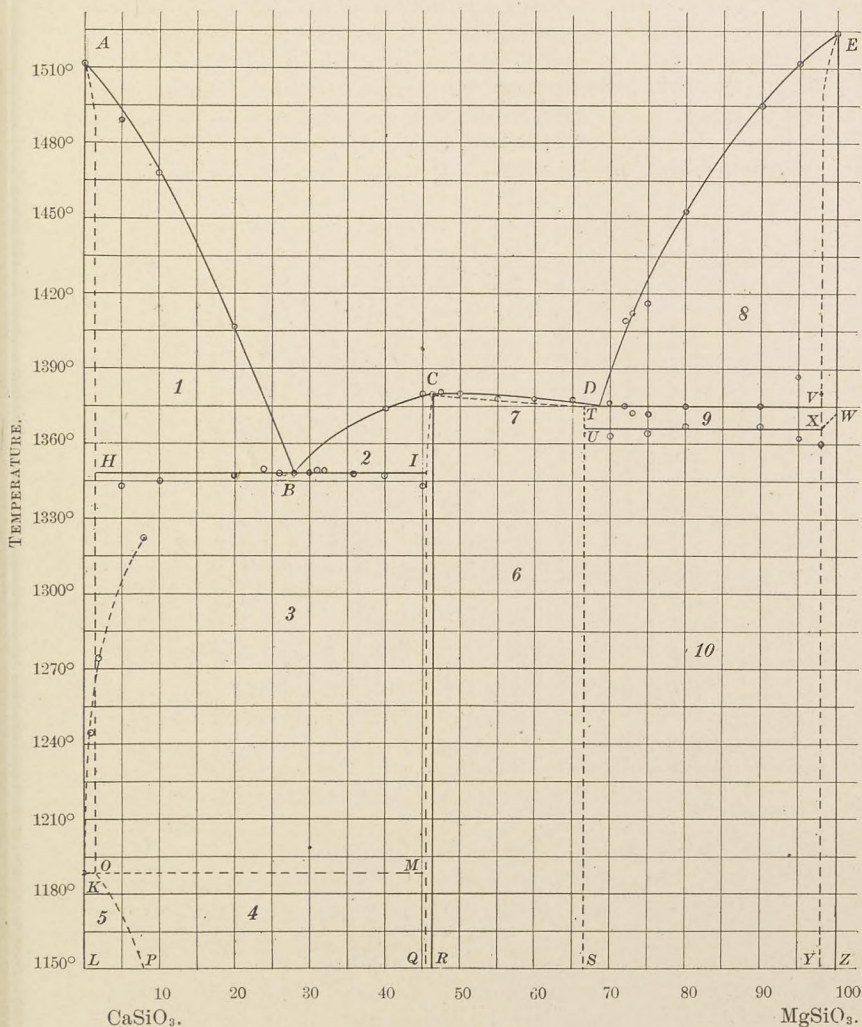
The end members, pseudo-wollastonite and diopside, and also the eutectic mixture, melt at a single temperature, with the reservation just made; that is, as sharply as we have yet observed with any silicate. The other mixtures show two phenomena: (1) the melting of whatever amount of eutectic is present in the mixture; and (2) as the temperature rises, the gradual solution in the melted eutectic of the excess component (diopside or pseudo-wollastonite, as the case may be), which lasts till the melting point curve ABC is reached. The temperature-time curves clearly show continuous change in character from the end members to the eutectic composition. Near the end member the predominant phenomenon is the upper point, which resembles the sharp melting of the pure component itself; the eutectic melting is of course small. It is clearly distinguishable, however, even when the mixture contains less than 1 per cent of eutectic. In mixtures farther from the end members in composition, the absorption of heat immediately above the eutectic melting is perceptible, and the highest point gradually takes on more and more the character of the end of this absorption and less and less that of a separate and independent melting point. Although, strictly speaking, this upper melting is always a solution, the temperature at which it terminates did not show, under the conditions described, any change with the rate of heating. In order to test this question, the rate was in several cases altered from 1° to 3° per minute, but the resulting effect on the upper point was less than the accidental errors of the separate determinations. As the eutectic composition is approached and the phenomenon has still more the character of a solution and less that of a melting, the upper point becomes less and less distinct.

Determination of the Eutectic Composition.—In the immediate neighborhood of the eutectic composition the difficulty of determining the upper point is still more increased by another phenomenon. The rapid temperature rise which immediately

TABLE II.
Temperature-Concentration Curve.

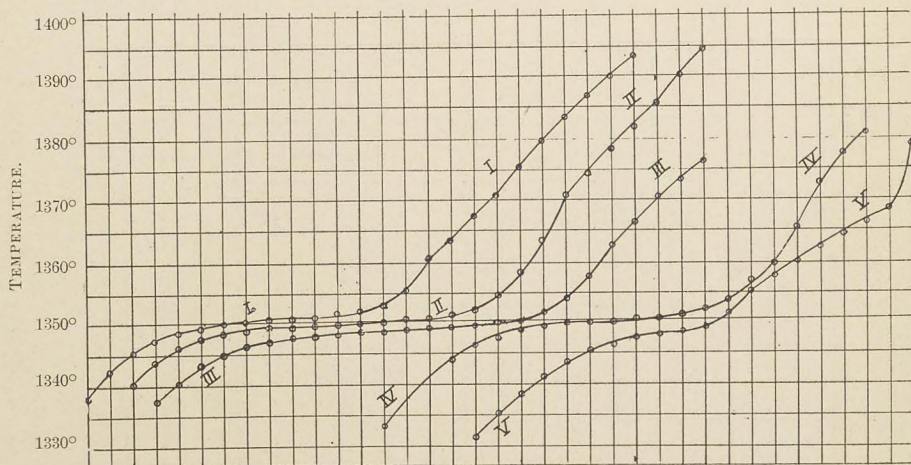
Weight% MgSiO ₃	Upper Point	Eutec- tic	Inver- sion	Weight% MgSiO ₃	Upper Point	Eutec- tic	Inver- sion
0	1510°	----	1190°	40	1374°	1347°	----
	1511	----	----				----
	1510	----	----	45	1380°	1343	----
	----	----	----				----
1	----	----	1245	46.3	1380	----	----
	----	----	----		1381	----	----
2	----	----	1273	----	1379	----	----
	----	----	----				----
5	1489	1343°	----	47.5	1381	----	----
	1481	----	----	----	1381	----	----
	1483	----	----				----
8	----	----	1327	50.0	1381	----	----
	----	----	----		1380	----	----
10	1468	1345	----				----
	1466	----	----	55	1378	----	----
	1466	1343	----				----
	----	----	----	60	1378	----	----
20	1405	1346	----	----	1377	----	----
	1397	1343	----				----
	1406	1347	----	65	1377	----	----
	1407	1346	----	----	1378	----	----
	----	----	----				----
24	----	1350	----	70	----	1376	1363°
	----	1350	----				----
	----	----	----	72	1409	1375	----
26	----	1348	----				----
	----	1348	----	73	1408	1373	----
	----	----	----	----	1412	----	----
28	----	1348	----				----
	----	1348	----	75	1416	1372	1364
	----	1348	----				----
	----	----	----	80	1452	1373	1367
30	----	1348	----	----	1453	1375	----
	----	1349	----		1452	----	----
	----	1349	----				----
	----	----	----	90	1495	1375	1367
31	----	1349	----		1484	----	----
	----	1350	----		1487	----	----
	----	1350	----				----
	----	----	----	95	1512	1387	1362
32	----	1348	----				----
	----	1349	----	98	----	----	1360
	----	1350	----				----
	----	----	----	100	1524	----	----
36	----	1348	----		1524	----	----
	----	1348	----				----

FIG. 1.



follows the principal melting now extends beyond the upper point and completely overwhelms it. The difficulty of determining a small residual melting is in striking contrast to the ease with which a slight absorption of heat can be detected below the principal melting.* Owing to this masking of the upper point, a direct determination of the eutectic composition is impossible by the ordinary method; that is, we cannot distinguish within several per cent the mixture which melts leav-

FIG. 2.



Temperature-time curves of mixtures in the vicinity of the eutectic composition (pseudo-wollastonite-diopside).

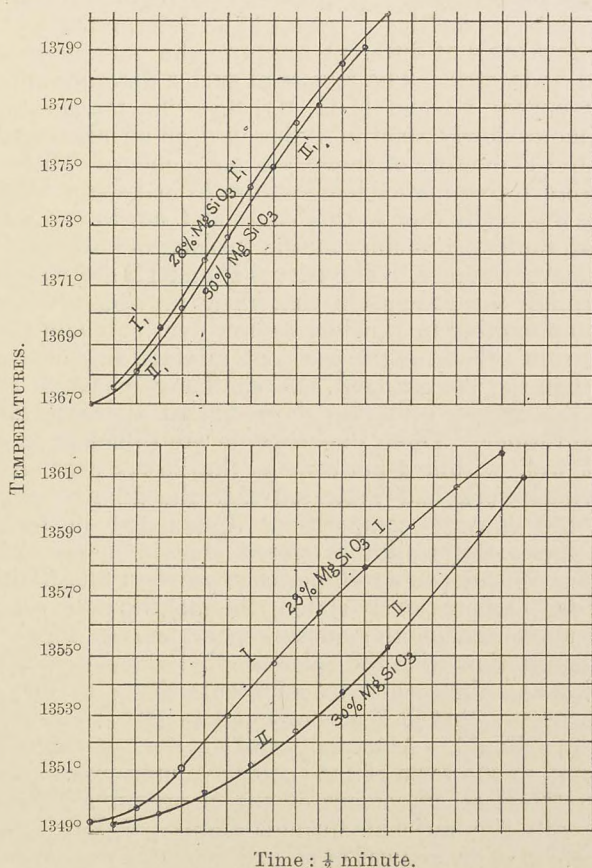
I. 24% MgSiO_3 . II. 26% MgSiO_3 . III. 28% MgSiO_3 . IV. 32% MgSiO_3 . V. 36% MgSiO_3 .

ing no excess component, since a number of mixtures appear to do so. This is well shown by the temperature-time curves in fig. 2, which were made with especial care with reference to this very point. The upper melting can hardly be distinguished in the 24 per cent mixture, though this contains over 8 per cent of the component in excess. (The point is in fact so faint that we could hardly distinguish it from the minute irregularities in the temperature curve of the furnace were it not for the fact that it lies on the curve ABC, fig. 1, which is well defined in other mixtures farther removed from the eutectic.) For locating the eutectic two methods still remain.

* It was undoubtedly the difficulty of detecting the upper points in this region and the failure to appreciate how easily such an experimental difficulty might arise which led R. Freis (*Neues Jahrb. Min., Beil. Bd. xxiii, 76, 1907*) to describe a similar series of melting points as forming a curve with the two inclined portions separated by a horizontal branch of considerable extent.

The first is to extrapolate downward the liquidus curves AB and BC in fig. 1, and take the mean of the points where they intersect the eutectic line HI. The accuracy of this extrapolation is limited by the uncertainty of the liquidus curve for some distance on each side of the eutectic composition. We found with these particular silicates that the results agreed to

FIG. 3.



Time: $\frac{1}{2}$ minute.

Location of the eutectic composition.

Curves I-I and II-II, 28 per cent and 30 per cent MgSiO_3 , just above the eutectic point.

Curves I'-I' and II'-II' the same at higher temperature.

5 per cent with a probable error of not over 2 per cent in the eutectic composition.

A more accurate determination seemed for some time to involve considerable difficulty, but a satisfactory solution of the

problem was finally obtained in the following way: Two small crucibles containing charges slightly different in composition were put together in the furnace and brought to such a temperature that the main eutectic melting was completed but the excess component, if any, still left undissolved. Then by suddenly increasing the furnace current and making alternate temperature readings of the two crucibles at intervals of 15 seconds, the relative heat absorptions in the region immediately above the eutectic melting point could be determined, and thus in a very few trials of different mixtures the eutectic composition could be located. The results of such a determination are shown in curves I-I and II-II, fig. 3. The temperature in II rises more slowly than in I, because of an absorption of heat due to the melting of the excess component. The curves were continued to a higher temperature to make sure that this difference was really due to this cause and not to the relative position of the two crucibles in the furnace or to some other accidental circumstance. The curves I' and II' are now parallel, confirming the conclusion that their previous divergence was due to a melting in II which is now over. It will be seen from this result that the 28 per cent mixture lies nearer the eutectic than the 30 per cent. A similar comparison of the 28 with the 26 per cent also showed that the eutectic lies nearer the former. These experiments are sufficient to locate the point well within 1 per cent at the 28 per cent mixture. The previous work had indicated that the 28 per cent was probably the eutectic composition. Calculated in terms of diopside, the eutectic mixture would contain in round numbers 60 per cent diopside: 40 per cent pseudo-wollastonite.

Diopside.—As previously stated, the melting-point of diopside is a maximum on the melting point curve, which fact, taken in connection with the microscopic homogeneity at this composition and the occurrence of a eutectic point on either side of it, proves that it is a compound in stable equilibrium with its own liquid. Abundant confirmation of this conclusion is found in the form of the specific-volume curve, p. 27, as well as in the close agreement of the composition of natural diopside with the rational formula $\text{CaSiO}_3 \cdot \text{MgSiO}_3$. As an example, we give an analysis of an exceptionally pure specimen from a metamorphosed limestone which occurs in Ham Island, Alaska. The composition of the *anhydrous* substance is also given for the sake of fairer comparison. This is justifiable, for the water is not chemically combined, a conclusion thoroughly established by the fact that the substance remains homogeneous as the water escapes.

	Diopside from Ham Island, Alaska	Cal. to the anhydrous condition	Cal. for CaSiO ₃ MgSiO ₃
SiO ₂ -----	54.65	55.46	53.63
Fe ₂ O ₃ -----	.13	.13	----
CaO -----	25.27	25.64	25.82
MgO -----	18.78	19.06	18.55
Na ₂ O -----	.03	.03	----
K ₂ O -----	.07	.07	----
H ₂ O -----	1.45	----	----
	<hr/> 100.38	<hr/> 100.39	<hr/> 100.00

When diopside is prepared by melting together lime, magnesia and silica in the proper proportions, it crystallizes readily, but not so rapidly as its constituents calcium and magnesium silicates, forming a dense white homogeneous mass with conspicuous cleavage. The optical constants, a full account of which is given in the second part of this paper, leave no room for doubt of the identity of the substance.

Measurable crystals was prepared by crystallizing this product from molten calcium chloride—Le Chartier's method.* This may be very conveniently done in platinum as described in a previous paper on magnesium silicate.† It is not possible, however, to perform the operation in hydrochloric acid gas, as was there done, for the diopside is then decomposed into calcium chloride, tridymite and magnesium pyroxene. The last two products were identified optically without difficulty. The calcium chloride should first be melted in the sealed crucible, traversed by a stream of dry hydrochloric acid gas. Then after the crucible has been cooled and the hydrochloric acid replaced by dry air, the crucible is unsealed and the silicate quickly introduced. In this operation some moisture doubtless gets in. Before heating again, dry indifferent gas is introduced. The crucible is heated for a number of days, the entering and exit tubes being guarded by driers. When the operation is completed, the excess of calcium chloride is removed by water. The product is usually in the form of transparent crystals of rhombic habit which sometimes attain to dimensions of several millimeters. The planes are often slightly coated with a thin film of what is probably calcium hydroxide, which doubtless comes from the decomposition of calcium chloride by the water vapor which could not be entirely excluded. It gives a strong alkaline reaction and may be readily removed with a little dilute HCl. Analysis shows that no lime is dissolved by the crystals, though they are not quite free from chlorine.

* Comptes Rendus, lxvii, 43, 1868.

† This Journal, xxii, 389, 1906.

	Found	Cal. for CaSiO ₃ , MgSiO ₃
SiO ₂	55.59	55.62
CaO	25.73	25.83
MgO	18.61	18.55
Fe ₂ O ₃ etc.18	---
Cl	trace	---
	<hr/> 100.11	<hr/> 100.00

Several products made in this way were united and tested in a mixture of methylene iodide and benzene to see if all was of uniform specific gravity. A small fraction, containing some of the larger crystals, floated, while the rest sank. These crystals seemed to differ from the rest only in porosity. The remainder were then divided into two fractions of only slightly different density and the specific gravity of each was determined by the pycnometer.

1. Lighter fraction	$\frac{\text{Sp. gr. at } 25^{\circ}}{\text{H}_2\text{O at } 25^{\circ}} = 3.270$
2. Heavier "	" 3.275
3. Natural diopside from Ham Island, Alaska,	" 3.268

An idea of the expansion of the diopside in the process of melting may be obtained by comparing this constant with the specific gravity of the glass of the same composition:

$$\frac{\text{Glass at } 30^{\circ}}{\text{H}_2\text{O at } 25^{\circ}} = 2.830.$$

The description and angular measurements of these crystals are to be found in Part II of this paper.

Melting Point Curve from 46.3—100 per cent MgSiO₃.—Referring again to fig. 1, it is seen that beyond 46.3 per cent MgSiO₃, the addition of it lowers the melting point gradually but very slightly, until about 68 per cent has been reached. Near this point there is an abrupt rise, the curve finally terminating at 1524°, the melting point of magnesium silicate. On the first branch of the curve (46.3–68 per cent) mix crystals of magnesium silicate in diopside separate. This conclusion was tentatively reached in the preliminary thermal work when it was found that the addition of a large percentage of magnesium silicate lowered the melting point of diopside very little, while the mixtures continued to show but *one* absorption of heat. The thermal evidence was subsequently confirmed by the specific volume curve, and by a very elaborate microscopic study.

Solid solution determined by microscopic homogeneity extends as far as 66.5 per cent MgSiO_3 : 33.5 per cent CaSiO_3 . The solid phases separating on the branch of the curve DE were found to be the mix-crystal just mentioned, and α - MgSiO_3 in all cases. All the mixtures from about 68–95 per cent MgSiO_3 showed an absorption of heat at 1375° . This is evidently a eutectic line and there is no doubt that we have here a case of Roozeboom's mix-crystal Type V,* where each of two mix-crystals *lowers* the melting point of the other to a eutectic. Points on this line to the left of the eutectic point could not be located since the liquidus curve lies only 2° to 3° higher up. The eutectic composition is about 68 per cent MgSiO_3 : 32 per cent CaSiO_3 and consists therefore of about $\frac{32}{33.5} = 95.5$ per cent of the diopside mix-crystal and about 4.5 per cent of free α - MgSiO_3 (in which about 2 per cent CaSiO_3 or 3.7 per cent of diopside is dissolved).

Inversion of MgSiO_3 .—About 1365° pure magnesium silicate undergoes a reversible change into an orthorhombic form. The heat of transformation is small, and apparently the change does not all happen at once, but extends over quite an interval of temperature. This is the only satisfactory way of accounting for the fact that while a small absorption of heat is observed in most of the mixtures of magnesium silicate from 70 per cent on, in the pure substance and in the mixtures near 100 per cent MgSiO_3 it was entirely overlooked. The existence of a form stable above 1365° was proved by crystallizing a melt near the melting point, and then suddenly chilling the crystals in water. Thus the form was instantly brought into a temperature region where viscosity was great enough to prevent an inversion. The inversion temperature was determined approximately as follows: One tenth of a gram of the substance was placed in a small platinum tray shaped from a piece of platinum foil. This was suspended by a fine platinum wire inside the furnace. After the material was melted and crystallized near the melting point, the temperature was lowered to a given temperature and held there about a half hour. The furnace in which the heating was done was designed for calorimetric purposes, and had a removable bottom which was swung aside at the proper moment, when the suspension wire was instantly melted by an electric current, allowing the charge to drop into a basin of water. The results were as follows:

*Zeitschr. f. Phys.-Chem., xxx, 403.

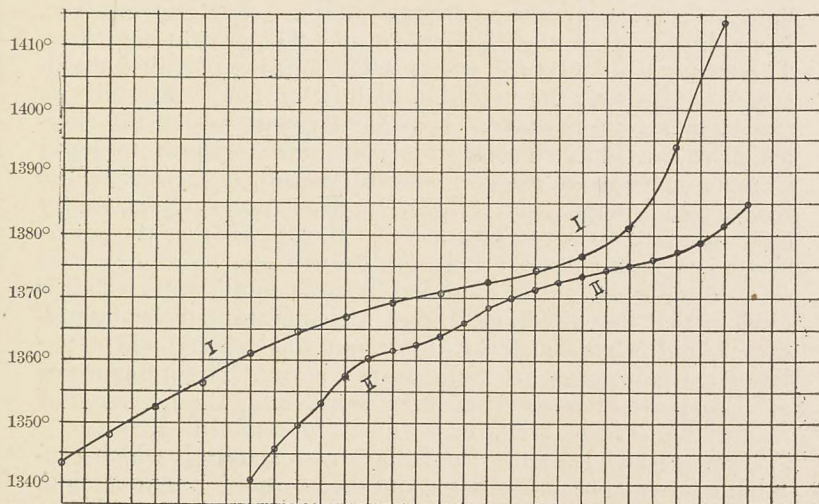
- 1 Chilled from an initial temperature of 1346° ; all orthorhombic crystals (α -form).
- 2 Chilled from an initial temperature of 1337° ; all the crystals were orthorhombic.
- 3 Chilled from an initial temperature of 1324° ; all monoclinic crystals (β -form).
- 4 Chilled again from 1324° with the same result.

After the existence of the α -form had been established, the inversion point was repeatedly sought for by the Frankenheim method and a very small minimum between 1405° and 1435° was found in many cases but by no means in all, and the point was so small that one might well have hesitated to interpret it as an inversion, had other evidence been lacking. Taken in connection with the sharp heat change which occurs in the mixtures (see below) at about 1365° , it appears that the inversion point is overstepped about 40° in both directions, which is in perfect accord with the sluggish behavior of solid silicates. The inversion point in pure magnesium silicate is represented in the diagram (fig. 1) as falling somewhat as it dissolves calcium silicate, because this is the relation which commonly holds, but it is manifestly impossible to settle the question at present.

α -Magnesium Silicate.—This form, which has already been described, crystallizes in the orthorhombic system in equant crystals on short doubly terminated prisms which resemble forsterite in habit, index of refraction and birefringence. Its specific gravity, judging from its index of refraction, varies little from that of β -magnesium silicate (3.192). It was found, by applying the floating method to a single small crystal, to be about 3.16. Fortunately, in several instances a few well-formed, separately developed crystals were found on the surface of charges of magnesium silicate which had been melted and crystallized in the furnace, though usually all was completely inverted into the magnesium pyroxene. The measurements of these crystals which are recorded in Part II of this paper *prove conclusively that this is a form entirely distinct from forsterite or enstatite.*

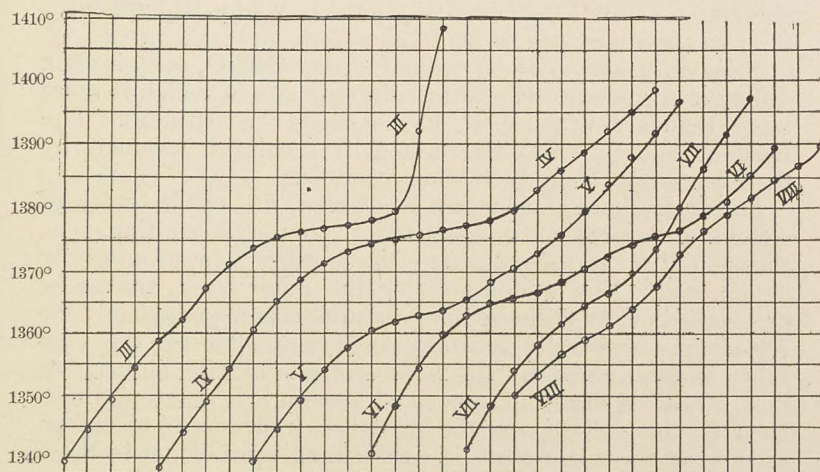
Inversion in the Mixtures.—The inversion line is traced in all the mixtures from 68 per cent to 98 per cent magnesium silicate and varies little from 1365° . Some typical curves showing both the inversion and eutectic points are plotted in figs. 4 and 5, curves II, V, VI, VII, and VIII. The significant feature of these curves is the gradual diminution of the heat absorption at the latter (eutectic) temperature and the gradual increase of that at the former (inversion), as we pass toward 100 per cent magnesium silicate. Thus in the 70 per cent mixture the eutectic melting is large, while in the 95 per

FIG. 4.



Temperature-time curves showing thermal behavior of mixtures rich in MgSiO_3 .
 Curve I-I, 60 % MgSiO_3 . II-II, 70 % MgSiO_3 .

FIG. 5.



Temperature-time curves showing thermal behavior of mixture rich in MgSiO_3 .
 Curve III. 65 % MgSiO_3 .

" IV. 75 % MgSiO_3 crystallized below 1300° by heating the glass.

" V. 75 % " " not far below 1365° .

" VI. 80 % " " " " " "

" VII. 90 % " " " " " "

" VIII. 95 % " " " " " "

cent it is minute and in the 98 per cent can be no longer detected; while the inversion, small in the 70 per cent mixture, is much greater in the 90 per cent and 95 per cent mixtures. The 98 per cent mixture, where solid solution of calcium silicate begins, shows the inversion plainly but not so markedly as the 95 per cent mixture. It evidently partakes of the character of the pure silicate, which is more resistant to rapid change. Dissolved calcium silicate therefore *facilitates* the inversion of magnesium silicate, while, as we shall presently see (page 20), dissolved magnesium silicate *hinders* the inversion of calcium silicate. It is not strange that the properties of a substance should be modified by solid solution, though it is evident that the direction of such a change cannot yet be predicted, but why an excess of foreign solid should affect the inversion point of a substance is not clear. The influence of solid diopside in concentrating or sharpening the inversion of magnesium silicate, however, seems to be established.

Curves I and III show the behavior of materials which contain no free magnesium silicate and therefore show no inversion. Curve IV shows what happens when mixtures are chilled to glass and then heated. Crystallization then leads to *enstatite*, which *evolves* heat slowly over a long range of temperature. Since this evolution covers the region above 1300° , the small absorption at 1365° is effectually hidden, where, as explained, the inversion seems to be lengthened out.

Solid Solutions.—The system $\text{CaSiO}_3\text{--MgSiO}_3$ contains six different series of solid solutions, in only two of which is there more than a few per cent of the smaller constituent. The limit of solubility was determined by the thermoelement, by the microscope or by both when possible.

So far as thermal tests are concerned, the results refer of course to the presence or absence of a eutectic melting, i. e., the solubility at the eutectic temperature is approximately determined. The microscope, on the other hand, makes its determinations at ordinary temperatures, where presumably the solubility is generally greater. In almost all cases the solubility as determined by the microscope is a little higher, but how far this is a real difference and how far it is due to a difference in the delicacy of the methods, it is unsafe to say on account of the uncertainty in establishing equilibrium in these solid silicate solutions; in other words, it is impossible to say whether a given solution is saturated or not. In the diagram, fig. 1, we have drawn the lines straight with a single exception, where we have more evidence that solubility increases with falling temperature.

1. Diopside in $\alpha\text{-MgSiO}_3$. On account of the difficulties involved, this series was not investigated.

2. Diopside in β - MgSiO_3 . The microscope detected inhomogeneity in the 3 per cent CaSiO_3 mixture, but none in the 2 per cent. No eutectic was observed in the latter. We may therefore put the solubility as 2 per cent CaSiO_3 , or 3.7 per cent diopside.

3. MgSiO_3 in diopside. The microscope places the limit of solubility at about 66.5 per cent MgSiO_3 : 33.5 per cent CaSiO_3 , i. e., the quantity of diopside in the saturated mix-crystal would be $33.5/53.7 = 63.4$ per cent. In other words, diopside is capable of dissolving $37.6/62.4 =$ more than 60 per cent of its own weight of magnesium silicate. This remarkable series of mix-crystals strongly resembles diopside. The optical work described in detail in Part II shows that the extinction angle and the optic axial angle both fall about $\frac{1}{2}^\circ$ for each additional per cent of magnesium silicate. The specific volume curve (fig. 9) shows that the solution is attended by expansion.

4. Calcium silicate in diopside. The microscope detected inhomogeneity at 44.5 per cent MgSiO_3 , while the thermoelement detected a plain eutectic in the 45 per cent MgSiO_3 . The limit of solubility is doubtless small, certainly less than $100 - 45/46.3 = 3$ per cent CaSiO_3 .

5. Diopside in α - CaSiO_3 (pseudo-wollastonite). Mixtures containing as much as 3 per cent MgSiO_3 plainly showed inhomogeneity when examined by the microscope. The inhomogeneity took the form of irregular bands, irregularly distributed, which showed a distinctly lower birefringence than the rest. The 2 per cent MgSiO_3 solution showed traces of the above structure and gave a plain eutectic when examined thermally. The 1 per cent solution is microscopically homogeneous and gives no more than a suspicion of a eutectic. The error will be slight if we put the limit of solubility at about 1-2 per cent MgSiO_3 , or in round numbers, 3-4 per cent of diopside.

6. Diopside in β - CaSiO_3 (wollastonite). In this case a thermal test is obviously useless. The microscopic analysis showed that solution ceased at about 17 per cent diopside (8 per cent MgSiO_3). Crystallization took place at about 1058° . The crystals of diopside and wollastonite are both monoclinic and the latter resembles diopside more closely than pseudo-wollastonite, so that it is not surprising that wollastonite should dissolve diopside in large quantity.

These solutions showed a very interesting behavior when they were heated. To understand this clearly, it should be remembered that the eutectic between pseudo-wollastonite and diopside melts at about 1348° , while wollastonite has an inversion point at about 1190° . Upon heating crystals of wollaston-

ite carrying 1 per cent MgSiO_3 (2.1 per cent diopside) for one hour at 1221° , no change was apparent. Heated again for two hours at 1245° , the inversion was slight. The inversion point of wollastonite appears, therefore, to be raised 40° – 50° by the solution of only 2 per cent diopside. (See p. 18.)

Since time is an important factor in sluggish changes, a direct comparison was made between pure wollastonite and two mix-crystal preparations of this series by heating all three in the same furnace for the same length of time, viz., 1 hour. The temperature ranged from 1257° to 1263° , i. e., about 65° above the inversion point of wollastonite. The wollastonite was completely inverted, the 2.1 per cent solution slightly inverted, while in the 4.3 per cent solution (2 per cent MgSiO_3) it was doubtful if any change at all had taken place. The two solid solutions were now returned to the furnace and held an hour longer between 1273° and 1300° , about a hundred degrees above the inversion point of pure calcium silicate. The weaker solution was now found to be much changed, the stronger one less so. The 8 per cent solution of MgSiO_3 , containing 17.3 per cent diopside, was heated for an hour at 1278° to 1280° , 90° above the inversion point of calcium silicate. A careful microscopic examination of the crystals then showed a considerable change in their appearance; a new product had separated but it did not show the characteristics of pseudo-wollastonite. Such optical properties as could be measured in fine-grained material (index of refraction, birefringence) agreed with diopside. This indicates that the solubility of diopside in wollastonite is greater at lower temperatures where the crystallization occurred, or perhaps that the solid solutions, being formed by rapid crystallization, were supersaturated. In either case the excess separates when the solution is heated to higher temperature.

Heated an hour longer at a temperature of 1298° – 1303° , more diopside separated, but the signs of inversion were still doubtful. Again, the crystals were returned to the furnace and the heating continued another hour at 1327° – 1343° . This time inversion was evident. These experiments show either a marked rise in the inversion temperature of wollastonite or else a great increase in molecular sluggishness caused by the dissolved diopside.

A brief discussion will make it clear under what conditions an inversion point may be raised and thus help to decide whether we have a real rise in the inversion temperature or not. By a thermodynamic method Beckman* has shown that the freezing or inversion point of a substance is changed by

* Ostwald's *Lehrbuch der Chemie*, vol. 2, pt. 2, pp. 38, 68.

TABLE III.

Inversion Temperature of Wollastonite-Diopside Mix-Crystals.

(Inversion point of wollastonite, 1190°.)

No. of Exper.	Composition	Time of Heating	Temperature	Results.
1	1% MgSiO ₃ (2.1% diopside)	1 hr.	1221°	No change.
2	1% MgSiO ₃ (2.1% diopside)	2 hr.	1245°	Inversion slight.
	Continuation of Exper. 1			
	0% MgSiO ₃			Completely inverted.
3	1% MgSiO ₃ (2.1% diopside)	1 hr.	1257-1263°	Slightly " Doubtful
	2% MgSiO ₃ (4.3% diopside)			
4	{ 1% MgSiO ₃ (Continuation of Exper. 3) }	1 hr.	1273-1300°	{ Largely inverted
	{ 2% MgSiO ₃ of Exper. 3) }			{ Much less "
5	8% MgSiO ₃ (17.3% diopside)	1 hr.	1278-1280°	Separation of diopside. No inversion.
6	8% MgSiO ₃ (17.3% diopside)			
	(Continuation of Exper. 5)	1 hr.	1298-1303°	Inversion doubtful.
7	Continuation of Exper. 6	1 hr.	1327-1343°	" evident.

FIG. 6.

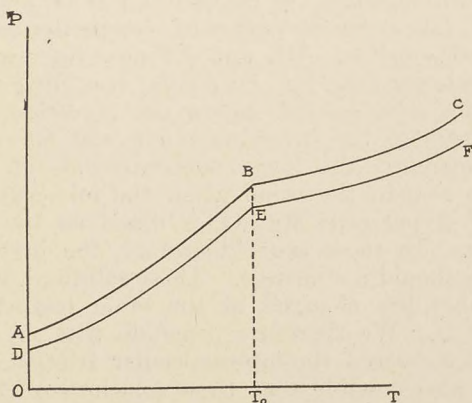


FIG. 6 shows under what conditions an inversion point remains unaltered after the formation of a solid solution.

the solution of another substance according to the equation

$$\Delta = \frac{0.2 T^2}{e} (C_1 - C_2)$$
 where Δ = the depression in the temperature, T = the absolute temperature of the inversion point in the pure substance, l = its latent heat of fusion, C_1 = the concentration of the solution above the inversion point and C_2 = the concentration of the solution below the point.

This formula holds approximately for concentrated solutions. When $C_1 = C_2$, i. e., when the concentration of the solid solution is not changed by the process of inversion, there will evidently be no change in the inversion point; when $C_1 > C_2$, the temperature will fall, but if C_2 , the concentration below the freezing point, is greater, then Δ will have the opposite sign, and the freezing point will be higher than that of the pure substance.

The same conclusion is reached by a graphic method.* In fig. 6 let AB represent the vapor pressure curve of the pure solid below the inversion point, BC the vapor pressure above it, and T_0 the inversion temperature. Now if this solid forms a solid solution, the vapor pressure of the former will be lowered according to the concentration of the solution. Suppose that this is the same above and below the inversion point, and that the vapor pressures are lowered to the same degree in both. It is evident that the new curves DE and EF will intersect at the same temperature and the inversion temperature is therefore unchanged.

In fig. 7 let us suppose that the concentrations of the two solid solutions are unequal, the one below the inversion point being the more dilute. The curve AB will be lowered to DE and BC will fall to EF by reason of the greater concentration of the second solution. DE and EF now intersect at E, at a temperature lower than T_0 . By similar reasoning we conclude that when the solid solution below the inversion point is the more concentrated the inversion point will be raised. (See fig 8.) Apparently the lower concentrations of diopside in wollastonite remain the same when the mix-crystals invert, for about 1–2 per cent $MgSiO_3$ is dissolved by the pseudo-wollastonite. In these cases, therefore, the inversion point theoretically should not change. These solutions, however, are unquestionably less changed at the same temperature than wollastonite is. We therefore conclude that the solution of diopside has increased the intermolecular friction of the crystals. It is also possible that these solutions of wollastonite-diopside which are more concentrated than 1–2 per cent $MgSiO_3$ really have a higher inversion point than 1190° . If the crystals saturated at this temperature remain more concentrated in diopside than the pseudo-wollastonite is, this must be true. A decision cannot be reached until we have some sure method of establishing equilibrium. Day and Shepherd found that solid solutions of lime or silica in calcium metasilicate inverted to wollastonite on cooling. Since the pure metasilicate does not behave so, we naturally conclude that the internal friction was lessened by the lime or silica. Magnesium

* Bodländer, Neues Jahrb. Min., Beilage Bd. xii, p. 52.

metasilicate has no such influence. The 4.3 per cent of diopside in pseudo-wollastonite was cooled from 1209° to 1050° during a period of $1\frac{1}{2}$ hours without producing any change in the crystal form. In the diagram, fig. 1, we have drawn a

FIG. 7.

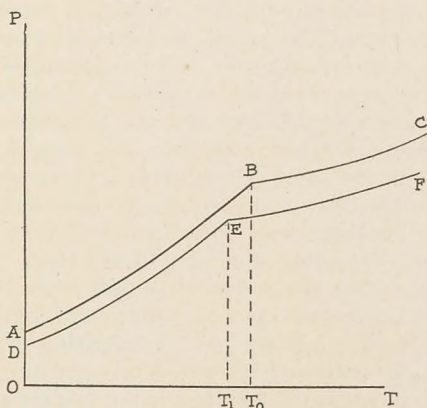


FIG. 7 shows under what conditions the inversion point of a solid is depressed after the formation of a solid solution.

dotted line through the points where this series of solutions was actually observed to invert, but it must not be accepted as a true inversion line. The inertia of these mix-crystals of wollastonite causes them to exhibit a curious and variable behavior

FIG. 8.

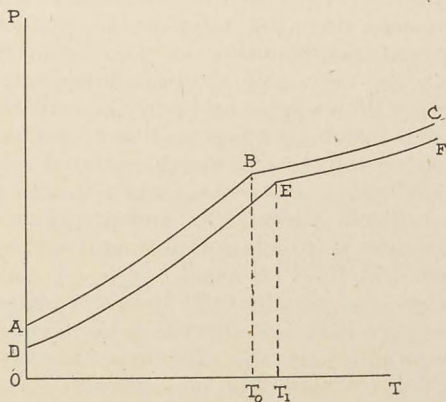


FIG. 8 shows under what conditions the inversion point is raised after the formation of a solid solution.

when heated, which in the beginning of the work was quite confusing. The normal behavior of a solution of wollastonite containing more than 2-4 per cent of diopside, (the limit of solubility of the latter in pseudo-wollastonite) would be as follows: First, an inversion should occur somewhat above 1190° , giving crystals of pseudo-wollastonite saturated with diopside, and an excess of free diopside. At 1348° some eutectic melting would be noted, and finally, when the melting point curve is reached, another thermal point would be found. Under ordinary experimental conditions, however, where the rate of heating is about 3° per minute, solutions containing 5 per cent MgSiO_3 (10.8 per cent diopside) showed no melting at the eutectic temperature. Evidently no inversion had taken place. When the rate of heating was considerably slower a slight eutectic melting was noted, while if the crystals were previously held for some time at 1360° , there was a strong absorption of heat at the eutectic temperature. In the 8 per cent MgSiO_3 solution (17.3 per cent diopside) the eutectic failed in one instance, i. e., there was no melting at the eutectic temperature. Mixtures of saturated mix-crystals of wollastonite-diopside give, when the heating is not too slow, three points, the eutectic at about 1348° , a further melting accompanying the inversion at a higher temperature,* and finally, the point on the melting point curve where all becomes liquid. Thus the 10 per cent mixture (containing about 4 per cent of free diopside) showed heat absorptions at 1340° , 1377° and 1451° . The 8 per cent solution showed a similar behavior, indicating that some inversion may have occurred below the eutectic points. Another explanation is perhaps more probable, viz.: that the lowest point may be due to an unstable eutectic between wollastonite and diopside, since the latter was found to separate from the more concentrated solutions at the higher temperatures. If so the point lies very near the pseudo-wollastonite diopside eutectic. A fact that seems to favor the explanation is that the 10 per cent solution always gives this lowest point although it has been proved that the more concentrated solutions invert with greater difficulty. Moreover, when the 28 per cent solution was crystallized below 1190° and therefore contained no pseudo-wollastonite (a conclusion also verified by the microscope), all melted at 1358° as usual.

Specific-volume curve.—In 1890 Retger† stated clearly two arguments to prove that diopside was a chemical compound in distinction from a mix-crystal. The first was that the minerals in nature which contain the metasilicates of calcium and

* Since the solution of the diopside in the wollastonite crystals prevents partly or wholly the eutectic melting at the proper temperature, this melting will at once occur when the crystals are inverted.

† Ann. Ecole Polytech. de Delft, iv, p. 186, 1890.

magnesium vary comparatively little from the compositions CaSiO_3 , MgSiO_3 and $\text{CaMgSi}_2\text{O}_6$; and the second, that the specific volume of diopside could not be calculated additively from the volumes of the constituents. Retgers's method of solving the question of isomorphism or isodimorphism between two substances is well known. It consists in the preparation of a suitable series of mix-crystals of the two substances and a study of the relation which their specific volumes bear to one another. He proved by many examples that the specific volumes of isomorphous mixtures (as he defined them), when plotted as a function of the composition, form a straight line. In the paper quoted above, Retgers said that this would be the best way to prove whether calcium and magnesium silicates form a double salt or are isodimorphous, if their mixtures could only be crystallized in sufficiently large individuals for specific gravity determinations. He used the floating method, which is not adapted for very small particles, and he emphasized the importance of making sure that the material is both physically and chemically homogeneous. He therefore used only transparent individuals for fear that aggregates might contain some foreign material which would escape optical detection. It has been shown in this laboratory that the specific gravities of mineral powders, if not *too* fine (100–120 mesh), can be determined with a degree of accuracy (± 0.01 for substances of the gravity of 3) very nearly as great as those obtained by Retgers's method. Of course, the particles should be free from air bubbles or vacua, and it must be admitted that powders require a very careful microscopic investigation to decide this point. Mixtures of calcium and magnesium silicate generally show a certain amount of "dustiness" due to very minute inclusions, or more probably to vacua. These are more numerous in the mixtures which are rich in magnesia (70–97 per cent), but not in the pure magnesium silicate itself. When large masses of material (100 grams) are crystallized slowly, the density is greater and the microscope shows that the vacua are fewer and smaller. Although the specific gravities of the mixtures crystallized in this way are still too low, we judged that they would probably be approximately comparable among themselves, and this conviction has been justified by experiment.

The specific-volume curve (fig. 9) plainly consists of three branches. AB is the locus of the volumes of mechanical mixtures of the pseudo-wollastonite and diopside (leaving out of the question the small mutual solubility). Independently of microscopic or thermal evidence, it would, of course, be impossible to say whether this line indicated a series of mechanical mixtures or a series of mix-crystals between two

isomorphous substances. In either case the volumes would form a straight line between the two constituents. DC is made up of diopside mix-crystals with magnesium silicate. The limit of the solubility of the latter in diopside is at about 70 to 72 per cent MgSiO_3 as determined by the specific volume

TABLE IV.

*Specific Gravities and Specific Volumes of Mixtures of
 CaSiO_3 and MgSiO_3 .*

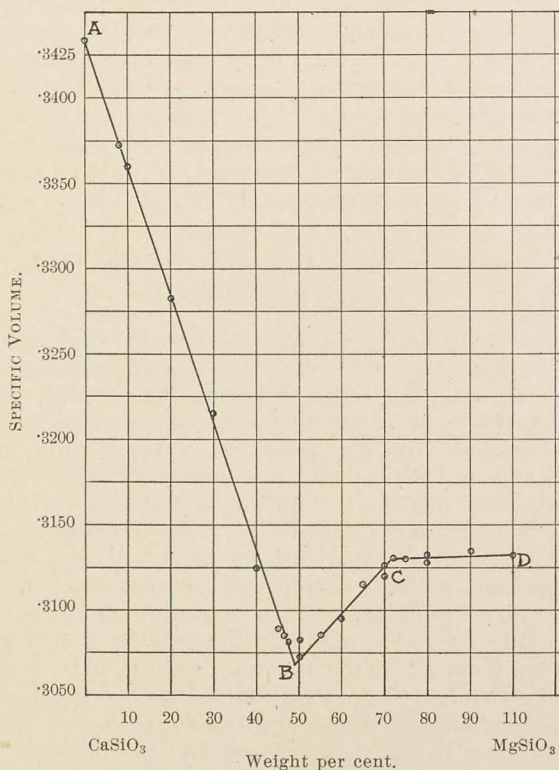
		Sp. gr.	Sp. v.
0%	MgSiO_3 -----	2.912	.3434
8	" -----	2.965	.3373
10	" -----	2.947	.3362
20	" -----	3.046	.3283
30	" -----	3.111	.3215
40	" -----	3.201	.3125
45	" -----	3.229	.3096
		3.237	.3089
46.3	" -----	3.236	.3090
		3.241	.3086
47.5	" -----	3.246	.3081
50	" -----	3.245	.3082
		3.255	.3072
55	" -----	3.241	.3086
		3.241	
60	" -----	3.229	.3096
65	" -----	3.211	.3115
		3.212	
70	" -----	3.205	.3120
		3.198	.3127
72	" -----	3.196	.3129
		3.196	.3127
75	" -----	3.194	.3130
80	" -----	3.198	.3127
		3.192	.3132
85	" -----	-----	-----
90	" -----	3.188	.3137
95	" -----	3.181	.3140
100	" -----	3.193	.3132

Where two different numbers are given, they belong to different preparations.

curve. The microscope sets the limit at about 66.5 per cent. The discrepancy is probably due to experimental error in the specific gravity determinations caused by the presence of bubbles in the grains. An inspection of the curve shows that the volumes of these solid solutions all lie above a line joining B and D. They are, therefore, greater than the volumes calcu-

lated on the assumption of a purely additive relation. A similar expansion is known in other cases.* CD contains the volumes of mixtures of magnesium silicate and the diopside mix-crystals. The minimum B, indicating a compound, falls at about 49 per cent MgSiO_3 instead of 46.3 per cent, which is demanded by the formula $\text{CaSiO}_3 \cdot \text{MgSiO}_3$. This is because a

FIG. 9.



melt of the latter composition forms a crystalline mass which always appears to contain more bubbles than the other compositions in its immediate neighborhood, so that the density of the crystals is not only *absolutely* but also *relatively* too low. It will be remembered in this connection that the diopside which was crystallized from calcium chloride had a specific gravity of 3.275, while that which was crystallized from a melt of the composition $\text{CaMgSi}_2\text{O}_6$ had a density of only 3.24.

* E. S. Shepherd, Journ. Phys. Chem., viii, 245, 1904.

We made a number of experiments with the intention of finding whether the mix-crystals of diopside and magnesium silicate could be crystallized again from calcium chloride, or if not, what change in composition they would show with varying quantities of the chloride, but the products obtained were not only not homogeneous, but the crystals were too small to separate from one another and the microscope was unable to identify them. One difficulty in these experiments was the impossibility of entirely excluding water from the apparatus. Its reaction with the calcium chloride, of course, formed some free lime, which was dissolved by the silicate. Pure diopside, as we have seen, does not dissolve lime, but magnesium silicate does. Three grams of the latter, containing only 0.12 per cent of lime, was crystallized* from calcium chloride and analyzed after the excess of the reagent was removed. It now contained 3.04 per cent of lime, an increase of 2.92 per cent.

PART II. *Optical Study*, by FRED. EUGENE WRIGHT and
ESPER S. LARSEN.

In the foregoing pages the theoretical aspects of the Ca-Mg-metasilicate problem have been treated at length, evidence from all sources, chemical, physical, optical and crystallographic, having been brought to bear on its solution. In this general presentation of the problem, however, only the more important and decisive optical and crystallographic data have been made use of, their detailed tabulation having been reserved for a separate section. In the following paragraphs those details which are still lacking are listed, and in order to avoid repetition, general theoretical considerations have been avoided so far as possible. In the attack on the present problem the effort has been made from the very first to combine the evidence from all viewpoints and to test each conclusion by such evidence. It has been found that by this method the constant interchange of ideas and the discussion of the details of the problem have tended greatly to improve and to strengthen the final result.

For the sake of convenience the optical and crystallographic features of the three compounds of this series will be considered first, after which will follow the particular features of the intermediate preparations.

Calcium Metasilicate.—The two enantiotropic forms of this compound, wollastonite and pseudo-wollastonite, have already been described in detail in this Journal† and the evidence need not be repeated at this point. Since the publi-

* The crystals were small but well-developed.

† This Journal, xxi, 103-108, 1906.

cation of the above paper, however, better facilities for refractive index determinations have been acquired and the refractive indices of the two compounds have been redetermined. The measurements were made on polished plates of the crystalline aggregate, experience having taught that even under such conditions it is possible to determine γ and α in sodium light with the reducing attachment of the Abbé-Pulfrich total refractometer, while β can also be ascertained if the individual grains are sufficiently large. For wollastonite the new values are, $\gamma_{\text{Na}} = 1.632 \pm .002$; $\beta_{\text{Na}} = 1.628 \pm .003$; $\alpha_{\text{Na}} = 1.616 \pm .002$; $\gamma - \alpha = .016$, $\gamma - \beta = .004$, $\beta - \alpha = .012$. The refractive indices of pseudo-wollastonite are: $\gamma_{\text{Na}} = 1.650 \pm .002$; $\alpha_{\text{Na}} = 1.609 \pm .003$; birefringence $\gamma - \alpha = .041$. The birefringence of both wollastonite and pseudo-wollastonite was furthermore checked by direct measurement in the thin section; $\gamma - \alpha$ for wollastonite being .014 and for pseudo-wollastonite .043.*

Magnesium Metasilicate.—Like the calcium metasilicate, this compound has also been described in a special paper in which the optical characteristics are considered together with the other properties. Four different forms or phases were there mentioned bearing monotropic relations to each other, the monoclinic Mg-pyroxene being the one stable form. In the course of the past winter, however, still another phase has been discovered, orthorhombic in symmetry and in general aspect and development not unlike that of olivine crystals.

TABLE V.

No.	Letter	Symbol	Miller	ϕ	ρ
1	<i>c</i> (?)	0	001	-- --	2° 00'
2	<i>a</i>	$\infty 0$	100	90° 00	90 00
3	<i>b</i>	0∞	010	0 00	"
4	<i>m</i>	∞	110	44 04	"
5	<i>n</i>	$\infty 2$	120	23 07	"
6	<i>l</i> (?)	$\infty \frac{5}{2}$	250	17 56	"
7	<i>k</i> (?)	3∞	310	70 44	"
8	<i>r</i> (?)	2∞	210	66 54	"
9	<i>s</i>	$\bar{1}1$	$\bar{1}11$	43 20	38 58
10	<i>e</i>	$\bar{1}2$	$\bar{1}21$	24 58	52 11
11	<i>p</i>	$\bar{1}0$	$\bar{1}01$	90 00	29 09
12	<i>o</i>	1	111	46 48	40 21
13	<i>i</i>	12	121	28 30	53 10
14	(?)	$\frac{1}{3}0$	$\bar{1}03$	90 00	11 55
15	(?)	$\frac{1}{3}0$	103	90 00	12 55

* Opportunity may here be improved to correct several of the optical data in the paper on the Lime-Silica Series of Minerals (this Jour., xxii, 293-302, 1906). At top line of p. 297 read: $\alpha = 1.609 \pm .003$, $\gamma = 1.620 \pm .002$, instead of the values given; on p. 298, 11 lines from the top, $\varepsilon = 1.554 \pm .002$ and $\omega = 1.544 \pm .002$; on p. 299, 8 lines from bottom, 1.585 and 1.621; and 2 lines from bottom, $\alpha = 1.590$; on last line, p. 299, read .019 instead of .025.

The optical data of the monoclinic Mg-pyroxene form given in the above article can now be supplemented by more accurate figures in several instances; and at the same time several errors in the crystallographic data can be rectified. The β -MgSiO₃ is monoclinic and the observed form and measured angles are listed in Table V above.*

The reflexion signals from many of the faces were multiple and wide variations in the angles occur. The best average ratios from these values are about

$$p_0 = .58 \quad q_0 = .60 \quad e = .046 \quad \mu = 87^\circ 26' ; \text{ or} \\ a : b : c = 1.03 : 1 : 0.60 ; \beta = 87^\circ 26' ;$$

values which are closely similar to those for enstatite but less so for diopside. The variations are not such, however, as to preclude isomorphic relations between the two. The plane of the optic axes lies normal to the plane of symmetry and not in the plane of symmetry as in most pyroxenes†; the bisectrix c is inclined to the vertical axis e , 21.8° . The optic axial angle was measured on the universal stage and by means of the two screw micrometer ocular. Care was taken to select favorable sections and the probable error in each case was not large. The average of all good determinations by both methods is $2V = 53.5^\circ \pm 1^\circ$, or $2E = 96^\circ$. The overlapping of the twinning lamellae often causes abnormal variations in this optic axial angle and it proved a difficult matter to find suitable sections. Etch figures on the cleavage face were also obtained and will be considered later, together with the etch figures of the other members of this series.

The α -MgSiO₃, to which reference has already been made, crystallizes readily and is obtained by quenching the crystallized melt from temperatures above 1365° to prevent its inversion to the β -form. Once obtained it can be held for apparently an indefinite period at ordinary temperatures without inversion to the more stable β -form. The crystals are orthorhombic in symmetry and in certain positions bear strong resemblance to the characteristic crystal habit of olivine. On the surface of a melt held at 1510° and then chilled rapidly, several crystals, water-clear and sharply bound crystallographically, occurred, and three of them ($1 \times .5 \times .2^{\text{mm}}$) were measured

* Compare with Table II on page 393, vol. xxii, 1906, this Journal, in which several letters were unfortunately transposed, although the relations are correctly represented in the gnomonic projection plat on the same page.

† The relations of the different pyroxenes, particularly of the magnesium iron group, have been recently discussed in an interesting paper by W. Wahl (Die Enstatit-augite, Tschermak's Miner. Petrogr. Mittheil., xxvi, 1-131, 1907), who proposes the name clino-enstatite for the β -MgSiO₃ or magnesium pyroxene. The suggestion is a good one and may well be adopted, the two latter terms being long and cumbersome.

on the goniometer. The reflexion signals were not of the best and the angles of the table can be considered only approximately correct, an error of $\pm 15'$ being easily possible.

TABLE VI.*

No.	Letter	Miller	Symbol	ϕ	ρ
1	<i>b</i>	010	0∞	$0^{\circ}03'$	$90^{\circ}00'$
2	<i>m</i>	110	∞	$40\ 08$	$90\ 00$
3	<i>k</i>	011	01	$0\ 01$	$25\ 09$

From the angles the crystallographic constants can be calculated:

$$p_o = 0.40 \quad q_o = 0.47$$

$$\text{or} \quad a : b : c = 1.19 : 1 : 0.47.$$

The crystals are often tabular and prismatic in shape after 010 as indicated in fig. 10. In other cases the prism zone is less prominent and the crystals are of equant development. The forms *b*, *m*, and *k* were observed on all three crystals. Cleavage after 100, good.

The plane of the optic axes is the cleavage plane 100 and the acute bisectrix is *c*. The optical orientation is, therefore, $a = b$; $b = c$; and optical character +. The refractive indices were determined by the immersion method in refractive liquids; $\alpha = 1.641 \pm .003$; $\beta = 1.648 \pm .003$; $\gamma = 1.663 \pm .003$; $\gamma - \alpha = .022$; $\gamma - \beta = .015$; $\beta - \alpha = .007$. The birefringence $\gamma - \beta = .016$ was furthermore measured directly on a tabular crystal 0.182^{mm} thick by use of the Babinet compensator. The optic axial angle is large and was measured with the two-screw micrometer ocular on two sections showing an optic axis in the field of vision. The average of the two values thus obtained ($2V = 59.5^{\circ}$ and 61.0°) is about $2V = 60.3^{\circ}$ and $2E = 111^{\circ}$. The axial dispersion is fairly strong, $2V\rho > 2Vv$.

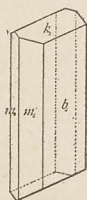


FIG. 10.

* The angles in the table are the averages of the different values obtained. These measurements were made on January 17, 1906, and since that time no suitable crystals for goniometric measurement have again been observed. Although the original notes stated definitely that these "crystal angles do not coincide with those of enstatite" while "the optical relations do not correspond with those of olivine," and this same form was observed at that time in at least seven different preparations, its importance was not realized and its presence was ascribed to impurity. In later experiments practically no chilling was done and not until the thermal data indicated to Dr. A. L. Day the presence of a high-temperature phase, enantiotropic to the first, were quenching experiments again resumed and with them the true significance of the α - MgSiO_3 became apparent.

In several of the larger crystals of the α - MgSiO_3 , a characteristic arrangement of inclusions and lines of growth was observed and strongly resembled the hourglass structure of certain pyroxenes, the hourglass portions of each crystal showing abnormal interference phenomena, due either to incipient changes into the β -form or to peculiar intergrowths or possibly, but not probably, to strain phenomena.

The α -form is readily distinguished from the β -form by its lack of polysynthetic twinning, parallel extinction and stronger birefringence; from olivine and enstatite by its cleavage and the position of the optic axial plane relative to the cleavage.

It is of interest to note that the α - MgSiO_3 , which is unstable below 1365° and cannot be obtained except under very special conditions, has not been observed in nature, thus establishing, as in the case of pseudo-wollastonite, a high temperature limit for the formation of certain minerals.

Diopside.—This third compound of the series is an excellent crystallizer and can be formed in a number of different ways and at different temperatures. The best crystals were obtained by heating glass of the composition $\text{CaMgSi}_2\text{O}_6$ in a flux of CaCl_2 in an atmosphere of dry HCl at 1000° for one week. The crystals varied in size up to 2^{mm} in diameter, were water-clear and of simple crystallographic habit. Three crystals were measured on the goniometer with reducing attachment. The reflexion signals obtained were not of the best and the values of Table VII are the averages of the observed angles. A number of other crystals were selected and mounted on the goniometer, but the reflexion signals from their faces were often multiple and unsatisfactory, and not suited to improve the results already obtained from the three measured crystals.

TABLE VII.

No.	Letter	Miller	Symbol	Artificial Diopside		Natural Diopside	
				ϕ	ρ	ϕ	ρ
1	<i>b</i>	010		0 00	90 01	0 00	90 00
2	<i>m</i>	110		43 30	90 00	43 33	90 00
3	<i>s</i>	$\bar{1}11$	-1	$\bar{2}4$ 51	33 04	$\bar{2}5$ 07	33 04
4	<i>x</i>	$\bar{2}21$	-2	$\bar{3}5$ 12	55 20	$\bar{3}5$ 22	55 19
5	λ (?)	$\bar{3}31$	-3	$\bar{3}9$ 17	66 17	$\bar{3}8$ 19	66 04

For the sake of comparison, the angular values ϕ and ρ for the same forms on natural diopside (Goldschmidt, Winkeltabellen, p. 283) are included in this table. From these angles the average value of $p_0 = .539$; $q_0 = .568$; $e = .276$, and $\mu = 73^\circ 59'$; or $a : b : c = 1.096 : 1 : .591$. For natural diopside, $p_0 = 0.5390$; $q_0 = 0.5670$; $e = 0.2731$; $\mu = 74^\circ 09'$; or

$a:b:c = 1.0934:1:0.5894$. Both the angular values and the calculated crystallographic constants prove the close resemblance of the artificial diopside crystals to the natural mineral, the differences observed being within the limits of error possible with the quality of reflection signals obtained from the artificial crystals. Except for the form λ , which was observed only once, the crystal habit is simple and requires no comment. Twinning after 100 is common and one of the three crystals measured was thus twinned, the twinning plane dividing the crystals into two nearly equal halves. Polysynthetic twinning after 100, however, occurred only rarely and is not characteristic.

Prismatic cleavage after 110 is good; in diopside crystallites from the melt indications of a parting after a dome or basal pinacoid face at an angle of about 66° with the prismatic cleavage cracks were also recorded.

The refractive indices were measured on polished plates of the crystalline material on the total refractometer in sodium light:

$$\gamma_{Na} = 1.694 \pm .002; \beta_{Na} = 1.671 \pm .002; \alpha_{Na} = 1.664 \pm .002$$

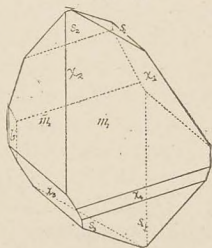
$$\gamma - \alpha = .030; \gamma - \beta = .023; \beta - \alpha = .007$$

Direct determinations of the birefringence were also made in the thin sections with the result: $\gamma - \alpha = .030 \pm .002$ (average of three measurements on good sections). The optic axial angle was measured on a number of different sections both with the universal stage and with the two-screw micrometer ocular. The average of four good determinations is: $2V = 59^\circ.3 \pm 1^\circ$; $2E = 114^\circ$. The optical axial dispersion is weak, $2V_\rho > 2V_v$. The plane of the optic axes is the plane of symmetry (010).

Extinction angles were measured both on the clinopinacoid and the prism face 110. On 010 $c:c = -38^\circ.5 \pm 1^\circ$. On 110 $c:c = -32^\circ.9 \pm 1^\circ$. The position of total extinction was ascertained in each case by use of the new bi-quartz wedge plate* and the values should be correct within 1° . Extinction angles were also measured for different faces in the prism zone. Suitable crystals, held in a specially constructed device,† were immersed in a liquid of the refractive index β and the extinction angle read for different angles of revolution of the crystal from its position of zero extinction when the orthopinacoid is normal to the axis of the microscope.

* This Journal, xxvi, 377-379, 1908. † This Journal, xxvi, 388, 1908.

FIG. 11.



ϕ^*	E	E_1
0°	0°	0°
10°	-13°	$-12^\circ.5$
20°	$-20^\circ.9$	$-21^\circ.7$
30°	$-27^\circ.1$	$-27^\circ.9$
40°	$-32^\circ.2$	$-31^\circ.9$
$43^\circ 30'$	$-32^\circ.9$	$-32^\circ.5$
50°	$-34^\circ.3$	$-34^\circ.6$
60°	$-35^\circ.5$	$-36^\circ.4$
70°	$-37^\circ.2$	$-37^\circ.6$
80°	$-38^\circ.5$	$-38^\circ.3$
90°	$-38^\circ.5$	$-38^\circ.5$

* ϕ =angle of prism face with orthopinacoid 100.

These figures indicate that for the first 40° from the orthopinacoid the extinction angle rises very rapidly while for faces near the clinopinacoid the variations are very slight.

For the sake of comparison the theoretical values of the extinction angles indicated by the Michel-Lévy formula* are listed under column E_1 .

From the melt diopside crystallizes readily, usually in the form of radiating prismatic individuals intricately intergrown and overlapping. A characteristic microscopic feature is the presence of fine bubble-like inclusions or cavities throughout the crystallized mass. These cavities are either tubular in shape and parallel in a general way the prismatic elongations of the crystallites; or they appear cutting across the sections in an irregular way not unlike the cavities in a section of worm-eaten wood. The cavities are probably due to the shrinkage accompanying the crystallization of diopside from the silicate melt.—Such air spaces in the crystals from CaCl_2 fluxes were only rarely observed and are not characteristic of the same.

The Intermediate Compositions.—In studying the preparations of this series intermediate in composition between the compounds, the microscopic analysis has been directed along two principal lines: (1) To ascertain whether or not the product is homogeneous; (2) to determine as accurately as possible the optic properties of the one or more components in each preparation. Experience with both thermal and optical data has shown that in certain instances limits of homogeneity cannot be detected within one or two per cent optically and the optical determinations of the limits of solid solution in this series given below may easily be in error therefore one or two per cent.

* Les Mineraux des Roches, p. 11, 1888. In this formula the following values were used: $V=29^\circ.6$, $\gamma=0^\circ$, ext. angle= $38^\circ.5$; or $\mu=8^\circ.9$, $\nu=68^\circ.1$; $u + v = 77^\circ$.

When out of the melt of a readily crystallizing substance, minute quantities of a second substance crystallize, they are usually so completely hidden in the mass of the first crystals that the process of finding them microscopically is not unlike that of "finding the needle in a haystack," particularly when the optical properties of the two substances are closely similar. It has been found by experience that the best method for detecting inhomogeneity is to immerse the powdered material (finely divided by tapping the substance in a mortar) in a liquid of the refractive index of the predominating substance; in this the minute particles of the second substance can be seen at a glance, if its refractive index be different from that of the first. For this purpose, a set of refractive liquids of indices ranging from 1.450 to 1.790 has been used, the refractive index of each successive liquid differing from the foregoing by .005. The refractive indices of these liquids were determined directly on an Abbé-Pulfrich total refractometer and their constancy checked every three months at least.* The liquids are kept in small dropping bottles (30^{cc} capacity) with ground glass stopper and ground glass cap, and the refractive indices of the liquids change either very slightly or not at all in three months.

In ascertaining the different optic properties of the members of this series, the following methods have been found most serviceable and seem best adapted to work of this character: Refractive indices were measured by use of refractive liquids after the immersion method of Schroeder van der Kolk. Wherever possible, especially on homogeneous preparations,

* The following is the list of liquids used in the preparation of this set. (On an average the change in refractive index of a liquid is about .001 for a change of 3° C. in temperature.)

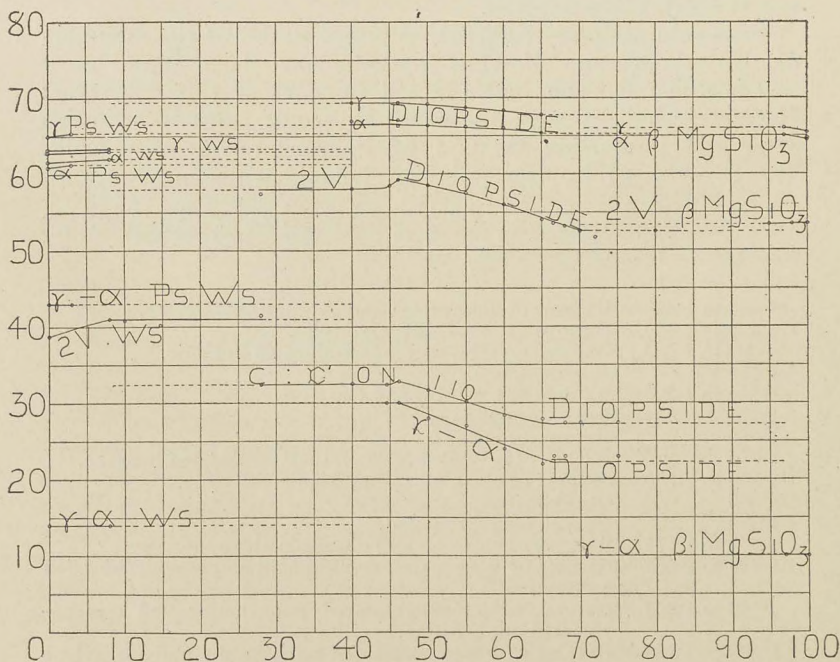
Refractive Index.

Liquids used.

1.450 to 1.465	Mixtures of chloroform and carbontetrachloride.
1.470 to 1.495	Mixtures of turpentine and xylol.
1.500 to 1.505	Mixtures of xylol and monochlorated benzene.
1.510	Aethyliodide.
1.515 to 1.520	Mixtures of cedar oil and clove oil.
1.525	Monochlorated benzene.
1.530	Mixtures of cedar oil and clove oil.
1.535	Mixture of aethylbromide and monochlorated benzene.
1.540 to 1.550	Mixtures of clove oil and cinnamic aldehyde.
1.555	Nitro-benzol.
1.560	Benzene monobromated.
1.565 to 1.615	Mixtures of clove oil and cinnamic aldehyde.
1.620 to 1.635	Mixtures of benzene mono-chlorated and α -monochlorated naphthaline.
1.640 to 1.655	Mixtures of α monochlorated naphthaline and α -monobromated naphthaline.
1.660 to 1.740	Mixtures of α -monobromated naphthaline and methylene iodide.
1.740 to 1.790	Mixture of methylene iodide and sulphur.

the refractive indices were measured directly on the total refractometer, experience having shown that with polished plates of the crystallized mass of substance the γ and α limiting refractive index lines can usually be distinguished if the reducing attachment be used. In such cases where the maximal and minimal indices are determined from aggregates of crystals rather than from one crystal, it is of course not possible to determine also the refractive index β . Optic axial angles were determined by use of the two-screw micrometer ocular and also by the modified universal stage* of Fedorow. Extinction angle measurements were made with the aid of the bi-quartz wedge plate,† care being taken to select favorable sections in each case. Direct determinations of the birefringence in the thin section or in flat crystal grains were accomplished by measuring the thickness of the plate or grain with the micrometer screw of the microscope (model Fuess) and then ascertaining the path difference of the emerging waves by means of a Babinet compensator. By this method only a fair degree of accuracy can be obtained because of the

FIG. 12.



* This Journal, xxiv, 317-369, 1907.

† This Journal, xxvi, 377-379, 1908.

difficulty of determining the thickness of the plates accurately. This error was reduced so far as possible by taking the average of a number of measurements of thickness on the same section and by grinding the sections thicker than usual.

The optical data prove that wollastonite can take up in solid solution about 17 per cent of diopside, while pseudo-wollastonite can absorb only about 4 per cent of diopside in solid solution; that in diopside only a small amount of the calcium metasilicate, not over 5 per cent, can enter into solid solution, while mixed crystals containing up to about 39 per cent of MgSiO_3 in diopside can exist; the maximal solid solution of diopside in $\beta\text{-MgSiO}_3$ is not great and does not exceed 5 per cent. These relations were ascertained both by observing the limit of homogeneity of the preparations and by observing the changes in the different optic constants of the preparations.

In fig. 12 the optic constants are represented graphically and the limits of solid solution are indicated by the breaks in the curves. The optical data from which these curves were drawn are included in the following table (VIII).

Although every effort was made to reduce the probable error of the values listed in this table, the very nature of the material precluded accuracy of a very high order. The refractive indices given in the table may be considered exact within ± 0.003 ; the direct determinations of birefringence within ± 0.003 , especially when checked by refractive index determination; the optic axial angles are not all of the same order of accuracy,—that of pseudo-wollastonite being the least satisfactory, with $\beta\text{-MgSiO}_3$ next; in general the probable error does not exceed $\pm 1^\circ$; the extinction-angle determinations on 110 probably vary less than 1° from the true values.

Table VIII as well as fig. 12 prove conclusively that diopside is a compound, and that the limits of solid solution for the different members of the series is that indicated above. Beginning with wollastonite, the refractive indices, the birefringence and the optical angle of the pure compound increase with increasing admixture of MgSiO_3 up to about 8 per cent MgSiO_3 , after which the curves are practically horizontal, thus marking the limit of crystal miscibility with diopside. In the sections free diopside was observed first in the preparation containing 10 per cent MgSiO_3 .—For pseudo-wollastonite the refractive indices, the birefringence and the optic axial angle increase slightly only up to about 2 per cent MgSiO_3 , and the examination of the preparations proved that beyond this limit inhomogeneity exists and diopside is present.—The limits of solid solution of CaSiO_3 in diopside were difficult to determine optically with any degree of certainty. The data indicate only slight solid solution, probably not below 45 per cent MgSiO_3 , or not over 2 per cent of calcium metasilicate. In the prepa-

TABLE VIII.

Composition % MgSiO ₃		<i>a</i>	<i>β</i>	<i>γ</i>	<i>γ</i> - <i>a</i> *	<i>γ</i> - <i>a</i>	<i>γ</i> - <i>β</i>	<i>γ</i> - <i>β</i> '	Opt. character	Optical axial angle 2 <i>V</i>	Dis- per- sion	Extinc- tion angles <i>c:c</i> on 110
0	Wollastonite -----	1·616	1·638	1·632	·014	·016	·004	·012	—	38°·8	<i>ρ > v</i>	----
0	Pseudo-wollastonite	1·609	--	1·650	·043	·041	--	--	+	7°·5	--	----
1	“	--	--	--	--	--	--	--	--	10°·0	--	----
3	“	1·612	--	1·654	·043	·042	--	--	--	--	--	----
5	“	--	--	--	--	--	--	--	--	10°·5	--	----
5	Wollastonite -----	--	--	--	--	--	--	--	--	38°·0	--	----
7·95	“	1·620	1·630	1·634	·014	·014	·004	·010	—	41°·0	--	----
7·95	Pseudo-wollastonite	--	--	--	--	--	--	--	+	7°·0	--	----
10	Wollastonite -----	--	--	--	--	--	--	--	--	40°·8	--	----
10·74	“	--	--	--	--	--	--	--	--	40°·2	--	----
28	“	--	--	--	--	--	--	--	--	41°·5	--	----
28	Diopside -----	--	--	--	--	--	--	--	+	57°·5	<i>ρ > v</i>	—32°·4
40	“	1·670	--	1·694	--	·024	--	--	--	58°·1	--	—32°·5
44·5	“	--	--	--	·030	--	--	--	--	--	--	—32°·4
45	“	--	--	--	--	--	--	--	--	58°·5	--	----
46·12	“	1·664	1·671	1·694	·030	·030	·023	·007	+	59°·3	--	—32°·8
50	“	1·664	--	1·692	--	·028	--	--	--	58°·5	--	—31°·7
55	“	1·662	--	1·684	·027	·022	--	--	--	57°·5	--	—30°·2
60	“	1·660	--	1·684	·024	·024	--	--	--	56°·0	--	—28°·4
65	“	1·654	--	1·678	·022	·024	--	--	--	54°·0	--	—27°·9
66·5	“	--	--	--	·023	--	--	--	--	53°·6	--	----
68	“	--	--	--	--	--	--	--	--	53°·2	--	—27°·4
70	“	--	--	--	--	--	--	--	--	52°·5	--	—27°·4
72	“	--	--	--	--	--	--	--	--	51°·7	--	----
75	“	--	--	--	·023	--	--	--	--	--	--	—27°·4
80	“	--	--	--	--	--	--	--	--	52°·5	--	----
90	“	--	--	--	--	--	--	--	--	--	--	----
95	“	--	--	--	--	--	--	--	+	53°·4	--	----
97	β-MgSiO ₃ -----	1·650	--	1·660	--	·010	--	--	+	--	--	----
98	“	--	--	--	--	--	--	--	--	53°·5	--	----
100	“	1·645	1·647	1·655	·009	·010	·008	·002	+	53°·5	--	----
100	α-MgSiO ₃ -----	1·641	1·648	1·663	--	·022	·015	·007	+	60°·3	<i>ρ > v</i>	----

* *γ*-*a* in this column was determined directly by measurements on plates in the thin section.

rations between 40 and 45 per cent peculiar phenomena were observed and no satisfactory tests of homogeneity could be made.—Between diopside and pure magnesium metasilicate mixed crystals extend from diopside up to about 66 or 67 per cent MgSiO₃ of the series. The appearance of all preparations between pure diopside (46·12 per cent MgSiO₃) and 67 per cent MgSiO₃ is that of diopside in the thin section so far as the optic properties are concerned. The refractive indices, the birefringence, the extinction angles and the optic axial angles all decrease gradually but noticeably, and the sections appear homogeneous under the microscope except for the minute air spaces. The crystallized melt changes noticeably moreover in appearance from the large, bright and glistening

aggregates of diopside to dull, lusterless, white granular masses of much finer grain and higher MgSiO_3 content.

Beyond the 68 per cent the preparations appear inhomogeneous, the $\beta\text{-MgSiO}_3$ appearing in increasing amounts as its composition is approached. In the preparations ranging from 68 to 90 per cent MgSiO_3 in composition, $\beta\text{-MgSiO}_3$ appears almost without exception intergrown with the diopside and usually occupies the center of the large diopside sections. The $\beta\text{-MgSiO}_3$ is invariably twinned polysynthetically after 100 and on sections approximately normal to the prism axis, the prismatic cleavage lines can be seen cutting across both the diopside and the $\beta\text{-MgSiO}_3$, thus indicating the close crystallographic symmetry of the two compounds. In such sections the $\beta\text{-MgSiO}_3$ is characterized by its weak birefringence and by the position of its optic axial plate parallel with the twinning lamellae, while for the enclosing diopside substance the optic axial plane is at right angles to the twinning lamellae.—The limit of crystal miscibility of diopside in $\beta\text{-MgSiO}_3$ is above 98 per cent MgSiO_3 , since preparations of that composition are clearly inhomogeneous. The optic properties of the $\beta\text{-MgSiO}_3$ change slightly between 98 and 100 per cent MgSiO_3 , but only enough to indicate very slight solid solution, probably not over 2 per cent of diopside.

Etch figures.—Proof of the fact of solid solution for compositions ranging from pure diopside to about 67 per cent MgSiO_3 was also gained by etching the crystals with hydrofluoric acid.

At the present time isomorphism is a much discussed subject and its final definition has not yet been agreed upon. Emphasis has been placed on similarity of the crystal form of the two end members, on analogous chemical composition, on complete miscibility, and on the fact that for some of the physical properties, as specific volumes, the properties of the intermediate mixtures are additive functions of those of the end members. This last assumption of Retgers has been questioned recently,* while the qualification of analogous chemical composition has long been considered unnecessary by certain investigators.

Briefly stated, the tendency seems to exist for crystallizing substances to absorb, during the process of crystallization, large or small amounts of other material. The more closely similar the absorbed material is to the absorbing crystal in crystal structure, dimensions and tendencies, the greater the amount in general which can be thus taken up. In certain instances, the properties of two substances are so similar and their molecular volumes so nearly equal, that the solid solution or crystal miscibility extends from the one compound without break to the second, and the physical properties vary continuously throughout the series. In such a case of complete miscibility no doubt can exist as to the isomorphic relations of the two end

* B. Gossner, *Zeitschr. Kryst.*, xlv, 417-519, 1908.

members. But in case the crystal miscibility is incomplete or limited the term isomorphism has not yet been defined with adequate precision nor the criteria therefor developed with sufficient sharpness to permit one to state in every actual case whether or not isomorphism does exist. It seems proper, however, to speak of the two compounds in the first case as completely isomorphous, while in other instances the isomorphism is incomplete or limited. In the case of incomplete isomorphism, criteria such as crystallographic similarity, additive character of certain physical properties in the intermediate mixtures, chemical analogy are then relied on to prove isomorphism.

In the present series, the diopside and β - MgSiO_3 are of the same crystal system and somewhat similar in crystallographic properties. Limited miscibility has been shown to exist and the physical properties prove that the two are incompletely isomorphous. This being the case, it is reasonable to suppose that their internal crystal structure is similar, that the distribution of the effective crystallographic forces is analogous. In the intermediate mixtures, therefore, the distribution of the forces is represented, approximately at least, by the resultants of the crystallographic forces of the end members in their proper intensities. One of the best methods for studying the distribution and relative intensity of crystallographic forces is by means of etch figures. On the above assumption, the etch figures of the intermediate members should be intermediate in character between those of the end members, diopside and β - MgSiO_3 .*

After considerable experimentation on the conditions best suited to produce favorable results, both with respect to the etch figures and the handling and photographing of the exceedingly small crystals, this statement has been substantiated. The etch figures on 110 were produced by immersing cleavage pieces from the different preparations in hot commercial hydrofluoric acid (heated over a steam bath in a platinum crucible) for 40 seconds and then stopping the reaction by plunging the crystal into cold water. The crystal was then mounted on the condenser lens attachment of the universal stage† and examined in strong reflected are light and turned until the proper cleavage face, 110, was normal to the axis of the microscope. The etch figures on 110 thus obtained were not of equal size or development for the different members of the series. The largest and best developed etch figures are those of diopside (Plate I, photomicrographs *a* and *b*), while the least favorable are those of β - MgSiO_3 , which are exceedingly difficult to obtain under

* The value of etch figures in determining isomorphism has been strongly advocated by Retgers (Zeitschr. f. Phys.-Chem., xvi, 35, 1895) and notwithstanding the objections which have been raised to this criterion, it does apply in certain series. In the present case of limited isomorphism the etch figures sustain the contention of Retgers.

† This Journal, xxiv, p. 342, and fig. 7, p. 332, 1907.

any conditions and are excessively small. The photomicrographs (Plate I), *a-f*, illustrate the changes in the shape of the etch figures thus produced on 110 in preparations ranging from diopside to pure $\beta\text{-MgSiO}_3$. The etch figures on diopside (*a* and *b*) are long spindle-shaped pits with an upper blunt termination. On an average their length is four times the width and the angle α between the two sides at their point of junction at the lower extremity is about 18° . These etch pits are similar in every detail to those on 110 of natural diopside from Ala,* Piedmont. Etch pits on the face 010 were also observed and likewise resembled those on 010 of the natural mineral.—The etch pits on 110 of the preparation 50 per cent MgSiO_3 (*c*) are very similar to the figures on diopside, the angle α between the two sides at the lower extremity being slightly greater perhaps. On crystals of the composition 55 per cent MgSiO_3 (*d*) the etch pits are noticeably wider and the angle α has increased to about 35° . This angle α gradually increases until at the limit of solid solution it measures approximately 50° (*f*). The relation of the length of the etch pits to their width changes from about 4:1 in diopside to 3:1 in the 55 per cent and about 5:3 at the limit as represented by the etch figures of the 75 per cent preparation, which were chosen in place of those of the 67 per cent because of the sharper definition of the particular figures photographed. The transitional changes in the shape of the upper portion of the etch figures are also characteristic. The etch figures on the cleavage faces of $\beta\text{-MgSiO}_3$ (*e*) are exceedingly small and triangular in shape; the angle α measures $55^\circ\text{--}60^\circ$ and the relation of length to width is about 3:2. Other details of the etch figures appear in Plate I and the evidence from all viewpoints tends to strengthen the assertion, that in this case of limited or incomplete isomorphism the character of the etch figures does change continuously with increasing MgSiO_3 , and in the direction of the type of the etch figures of pure $\beta\text{-MgSiO}_3$.

It is of interest to note that the $\beta\text{-MgSiO}_3$, the low temperature form, takes up very little if any diopside in solid solution. This may be due to the fact that the high temperature-, α -form, is orthorhombic and therefore would have less tendency to take up the diopside molecule.

On the calcium side of diopside the crystal miscibility in the series is very slight, diopside taking up only small amounts of the calcium metasilicate. Wollastonite, on the other hand, can absorb up to 17 per cent of diopside and still remain homogeneous, whereas pseudo-wollastonite takes only 4 per cent at most of diopside in solid solution. No satisfactory explanation has been found to account for these differences in the behavior of the different compounds of this series.

* Compare R. A. Daly, Proc. Amer. Acad. of Arts and Sciences, xxxiv, 373-428, pl. iv, No. 18, 1899.

In Part I of this paper, the fact of eutectic mixtures and its bearing on the present problem are shown to be of prime importance. In the case of alloys eutectic textures are definitely recognized and it is natural to expect such textures in silicate melts. In the latter, however, power and rapidity of crystallization, combined with viscosity, frequent absence of stable equilibrium, and other factors, tend usually to veil effectively such textures which might otherwise develop. Indications of probable eutectic textures were occasionally recorded in this series, but as a rule the crystallization apparently takes place so rapidly with strong undercooling that normal, theoretical conditions of equilibrium do not exist.

It is also of interest to note that throughout this series the melts of the pure compounds are, as a rule, of coarser grain than the intermediate compositions and of more vitreous luster. The intermediate mixtures frequently resemble porcelain in appearance. This change in aspect undoubtedly results from the decrease in granularity and lack of continuity of the single crystallites.

The inversion of the α - and β -MgSiO₃.—With pure MgSiO₃ melts the thermal data show practically no heat effect at the temperature of inversion of the β - into the α -form and vice versa, and only after the admixture of several per cent of diopside does the thermal effect produced by the inversion appear. The quenching experiments of Dr. A. L. Day, however, proved definitely that the α -MgSiO₃ did exist, and attempts were then made to fix the temperature of inversion by use of a specially constructed thermal microscope.* (Fig. 13, *a* and *b*.)

* Constructed in the workshop of the Geophysical Laboratory after plans by Dr. Arthur L. Day and the writer. The details of construction of the electric resistance furnace are given in fig. 13*b*, two important features of which were suggested by Dr. Day, namely, the enclosing of the whole in a suitable water jacket and the splitting of the thermoelement wires to serve as a support for the preparations. By this latter device the purity and temperature of the preparations even at high temperatures is insured. The microscope is fitted with revolvable nicols; at the base of the furnace there is a thin metal slide, A₃, by means of which part or all of the field can be shaded and the characteristics of the light emitted and transmitted by the body studied with respect to effects of polarization. A plate at high temperatures may become often self-luminous and it is then necessary to adopt special devices to detect transmitted polarized light and with this end in view the optical system of the microscope has been arranged. With it, also, the character of the emitted light alone can be examined with respect to polarization effects if such exist. At high temperatures the white heat of the furnace tends to veil the interference phenomena unless the transmitted light be of greater intensity, and this condition has been met by using an electric arc as source of light. With this furnace the birefringence of quartz has been measured up to 1300° and it is proposed to study the optical changes in several minerals at different temperatures in this way.—Temperature readings are made either roughly on a direct reading Siemens and Halske voltmeter or accurately by use of the potentiometer.—The water jacketing of the furnace permits its use on any microscope in which the distance between the stage and the objective can be made great enough, the optical system remaining thereby unchanged.

FIG. 13, a.

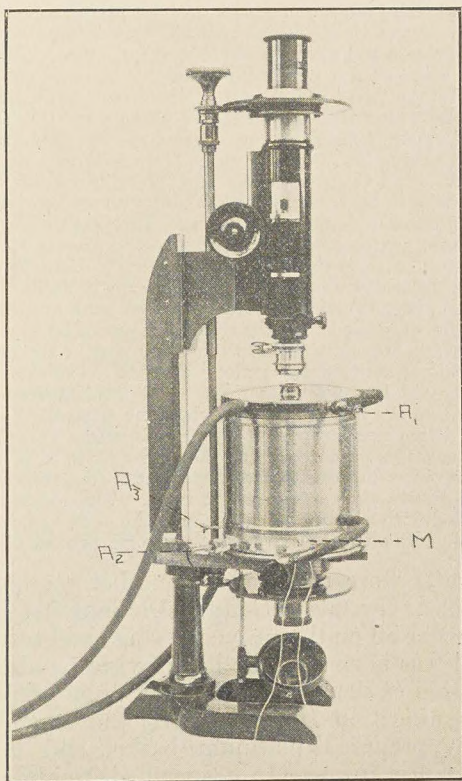
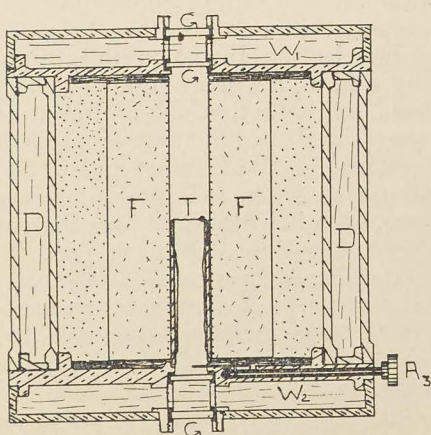


FIG. 13, b.



FIGS. 13, *a* and *b*.—Microscope equipped with electric resistance furnace. With the exception of the base and the upper tube, which were taken from a Fuess universal stage microscope, this thermal microscope was constructed in the workshop of the Geophysical Laboratory. The microscope is fitted with revolvable nicols and a low power 3-inch objective. The furnace rests directly on the stage of the microscope and can be revolved through small angles. Its different parts are shown in cross section in fig. 13*b* (one-half actual size). The water jacket consists of three parts; W_2 , base; D , side cylinder, and W_1 , cap. Each of these parts is complete in itself and by means of rubber tubing (fig. 13*a*) the water is made to pass through W_2 , then D and finally W_1 . At G in both W_1 and W_2 glass plates are introduced and allow light rays to be transmitted without permitting the heat to reach the objective and lower condenser system. The circulating water is sufficient to keep these plates cool. In the first experiments air bubbles from the water collected between the plates and seriously disturbed the clearness of vision. This difficulty was overcome by means of rubber plungers fastened to A_1 and A_2 (fig. 13) which could be passed back and forth in front of the plates and the bubbles brushed aside. By means of the rod A_3 with its attached brass plate, transmitted light from any part of the field can be shut off and the effects of emitted light alone studied. The furnace itself consists of a tube F (fig. 13*b*) 7.5 cm long, 4.5 cm outside diameter and 1 cm inside diameter, wound on the inside with fine platinum wire .35 mm diameter. The thermoelement wires are supported by the porcelain tube T , which rests directly on the asbestos paper covering the upper plate of W_2 . The thermoelement wires are introduced into the furnace at M (fig. 13*a*) and the furnace wires on the opposite side of the microscope. The sides of the furnace, F , are surrounded with magnesia powder and the ends capped with asbestos paper, to prevent loss of heat from radiation so far as possible.

Better results were obtained by another method, in which single, water-clear crystals of β - $MgSiO_3$ (about $.2 \times .2 \times 1$ mm) were mounted in cedar oil on the universal stage and turned until the clinopinacoid was normal to the line of vision and the twinning planes appeared as sharp lines. After photographing in this position (magnification 100 diameters) the crystal was placed in a specially prepared platinum basket and heated in an electric resistance furnace to a specified temperature, either above or below that of the β - $MgSiO_3$ inversion. After cooling, the crystal was again photographed under precisely the same conditions as before heating. The study of a long series of negatives prepared in this way has brought out several interesting points: In the inversion of a single crystal of β - $MgSiO_3$ to the α -form, no great volume change is involved nor even a great redistribution of the molecules. This is evident from the fact that after reversion from the α - to the β - $MgSiO_3$ the original crystal is intact and its faces still fairly sharp. Twinning planes are still present though usually in different positions, each lamella extending the entire length of the crystal as before heating. On such paramorphic change, inversion into one form and reversion to the original, it might be expected that, as in crystal aggregates formed by precipitation, many crystal nuclei would be formed,* and that on reversion each one of the new nuclei would produce at least one separate individual of the original form, with the result

*This actually happens on the inversion of wollastonite into pseudowollastonite. This Journal, xxi, 107, 1906.

that instead of a single crystal or a regularly twinned crystal, the aggregate of irregularly oriented individuals would result. In case, however, the molecular redistribution was slight, the inversion might proceed in regular fashion throughout the entire crystal and the effect of inversion and reversion be chiefly one of shifting of the ever present twinning lamellae. And this is the exact state of change in the β - MgSiO_3 crystals. Rarely the subdivision of a crystal into several irregularly bounded parts was noted and usually only the shifting of the lamellae. It was also of interest to observe that occasionally a shifting of the twinning lamellae took place in crystals heated to temperatures slightly below the inversion point. Because of this property, no decisive determinations of the inversion point could be made and recourse was taken to sudden chilling experiments—the preparations being first melted, the temperature then lowered and kept at a specified point for one hour, after which the preparation was dropped into cold water and chilled almost instantly. The α - MgSiO_3 thus obtained clearly showed the effect of incipient change even under these conditions, the major part of the powder being full of minute dustlike particles or cavities and as a result was semi- or sub-transparent, and only now and then were clear portions of the α -form observed. Whenever the α - MgSiO_3 was held at temperatures slightly below the inversion point and then quenched, the entire preparation consisted essentially of the twinned β -form alone in clear transparent individuals, the dusty effect as well as the α - MgSiO_3 aggregates having practically disappeared except for an occasional clear crystal of the same.

Summary.

1. The end members of the system CaSiO_3 - MgSiO_3 both exhibit enantiotropy. The inversion point in the former is about 1190° . The α -form, pseudo-wollastonite, is unknown in nature. The β -form is the mineral wollastonite. The β -form of magnesium silicate is the magnesian pyroxene occurring in meteorites and in intergrowths with enstatite and has recently been called clino-enstatite.* At about 1365° it is transformed into an orthorhombic form quite distinct from enstatite and unknown in nature.

2. Only one stable compound appears, viz., $\text{CaSiO}_3 \cdot \text{MgSiO}_3$, identical with diopside. It melts at 1380° and has a specific gravity of 3.275. It was obtained in well-formed, measurable crystals extremely pure, when crystallized from molten calcium chloride.

3. A eutectic occurs between diopside and pseudo-wollastonite at the composition 60 per cent diopside : 40 per cent calcium silicate. It melts at 1348° . A second eutectic occurs at about 68 per cent MgSiO_3 : 32 per cent CaSiO_3 . It is com-

* W. Wahl, Die Enstatit-augite, Tschermak's Mitth., xxvi, 1-131, 1907.

posed of about 95.5 per cent of a mix-crystal containing about 62.5 per cent of diopside, 37.5 per cent magnesium silicate, and 4.5 per cent α - MgSiO_3 . Its melting temperature is 1375° . Microscopically eutectic textures were observed rarely if at all.

4. Six solid solutions appear in this system. Only two of them contain more than three or four per cent of the lesser component, and only these will be mentioned here.

a. β -calcium silicate (wollastonite) forms a saturated solution of wollastonite containing about 17 per cent diopside (8 per cent MgSiO_3): 83 per cent CaSiO_3 , when crystallization takes place in the neighborhood of 1050° , i. e., wollastonite is capable of dissolving about $\frac{17}{83} = 20$ per cent of its own weight. This series

of solutions is interesting from the fact that the inversion point of pure calcium silicate (1190°) appears to be raised by the addition of MgSiO_3 , up to 100° in the most concentrated solutions. This is probably largely, if not wholly, an *apparent* rise in the inversion point due to viscosity, for, as is well known, an inversion point should be raised only when the concentration of the solution below the point is greater than that above, while here there is a rise in the weaker solutions which suffer no change in concentration when they invert. Again, the concentration of solutions just below the inversion point cannot be determined with accuracy on account of the difficulty of establishing an equilibrium in solid silicate solutions.

b. Diopside dissolves about 60 per cent of its own weight, forming a solution which contains 66.5 per cent MgSiO_3 : 33.5 per cent CaSiO_3 . This saturated solution is very similar to diopside in all its properties. Its melting point is only 3° lower (i. e., the maximum heat absorption falls there, the melting interval is unknown). The specific gravity changes very little; the optic data show slight but noticeable changes: the refractive indices, the birefringence, the optic axial angle and the extinction angles all falling continuously with the addition of MgSiO_3 from diopside up to the limit of solid solution at 66.5 per cent MgSiO_3 .

5. In the series of limited solid solution between diopside and clino-enstatite, the effect of the addition of MgSiO_3 to diopside is, furthermore, clearly shown by etch figures on the prismatic cleavage faces. On passing from diopside to the limit of solid solution at about 66.5 per cent MgSiO_3 , the shape of the etch pits changes gradually, their character, on preparations of intermediate composition, being intermediate between those of the two compounds, diopside and pure β - MgSiO_3 , thus proving that actual solid solution does exist in the series, and that the effects of the end members are felt crystallographically in the solid solutions of the same.—For the observation, under the microscope, of changes which take place in substances at high temperatures, a special micro-

scope, fitted with electric resistance furnace, fig. 13a, has been constructed and found useful in the study of these etch pits.

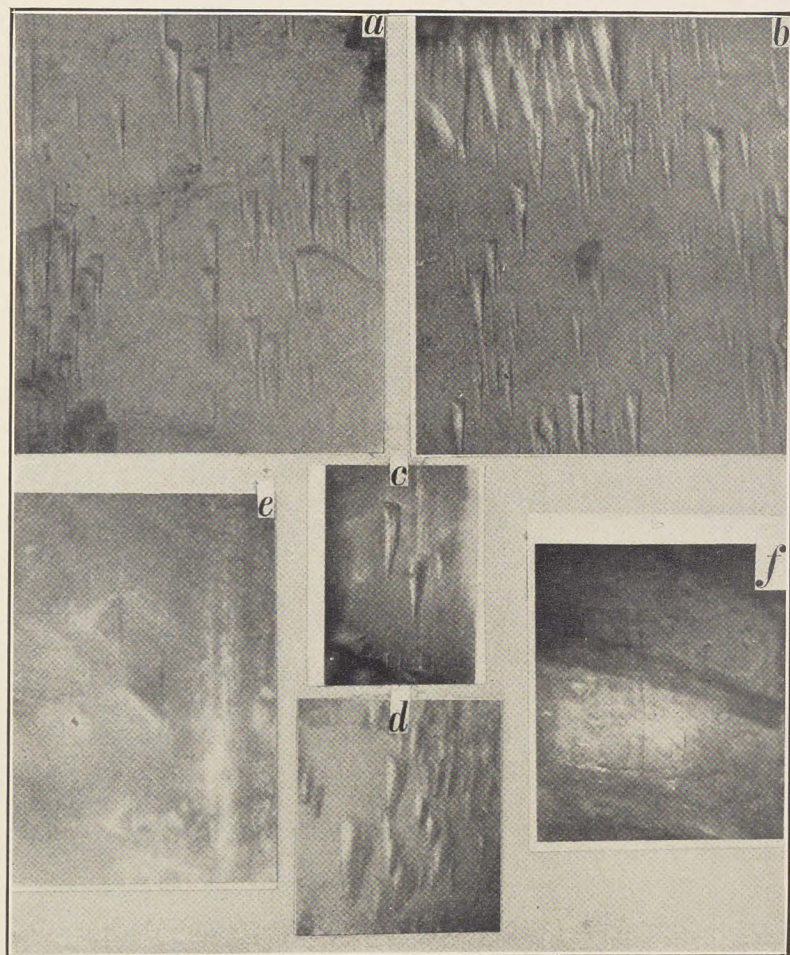
6. The specific-volume curve consists of three well-defined branches, the first of which is the locus of the volumes of mechanical mixtures of pseudo-wollastonite (α - CaSiO_3) and diopside; the second, that of the solid solutions of magnesian pyroxene (β - MgSiO_3) in diopside; and the third the locus of the volumes of mixtures of saturated mix-crystals just mentioned, and the free magnesian pyroxene. The volume of the solid solutions is *greater* than the sum of the constituent volumes. There is a sharp minimum on the curve at the composition of diopside CaSiO_3 . MgSiO_3 . On account of the presence of minute bubbles in the crystals and the comparatively small difference between the specific gravity of diopside and that of the magnesian pyroxene, the critical points on the curve are several per cent in error.

7. A method for the more accurate determination of the composition eutectics is described; also a method for the approximate location of inversion points in inert substances. The accidental variations between different determinations of the melting point of a sharp melting silicate seldom amount to 1° up to 1500° . This is the accuracy available for comparative measurements. The absolute accuracy of a determination is less than this on account of the present limitations of the absolute scale.

The authors wish to express to Dr. Arthur L. Day their hearty thanks for valuable assistance in connection with the study of the α -magnesium silicate.

Geophysical Laboratory, Carnegie Institution of Washington,
Washington, D. C., July 10, 1908.

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Photomicrographs.

a Artificial diopside. Etch pits on 110 produced by action of hot commercial HF for 40 seconds. Magnification 200 diameters.

b Artificial diopside. Etch pits on 110. Exposed to hot commercial HF 40 seconds. Magnification 230 diameters.

c Etch pits on 110 of crystal MgSiO_3 50 per cent, CaSiO_3 50 per cent. Time of exposure 40 seconds in hot commercial HF. Magnification 220 diameters.

d Etch pits on 110 of crystal MgSiO_3 55 per cent, CaSiO_3 45 per cent. Time of exposure in hot commercial HF, 40 seconds. Magnification 440 diameters.

e Etch pits on 110 Mg-pyroxene ($\beta\text{-MgSiO}_3$). Exposed 50 seconds in hot commercial HF. Magnification 1065 diameters.

f Etch pits on 110 of crystal MgSiO_3 75 per cent, CaSiO_3 25 per cent. Exposed 40 seconds in hot commercial HF. Magnification 230 diameters.



